

# The Journal *of the* Society of Dyers and Colourists

Volume 76



Number 6

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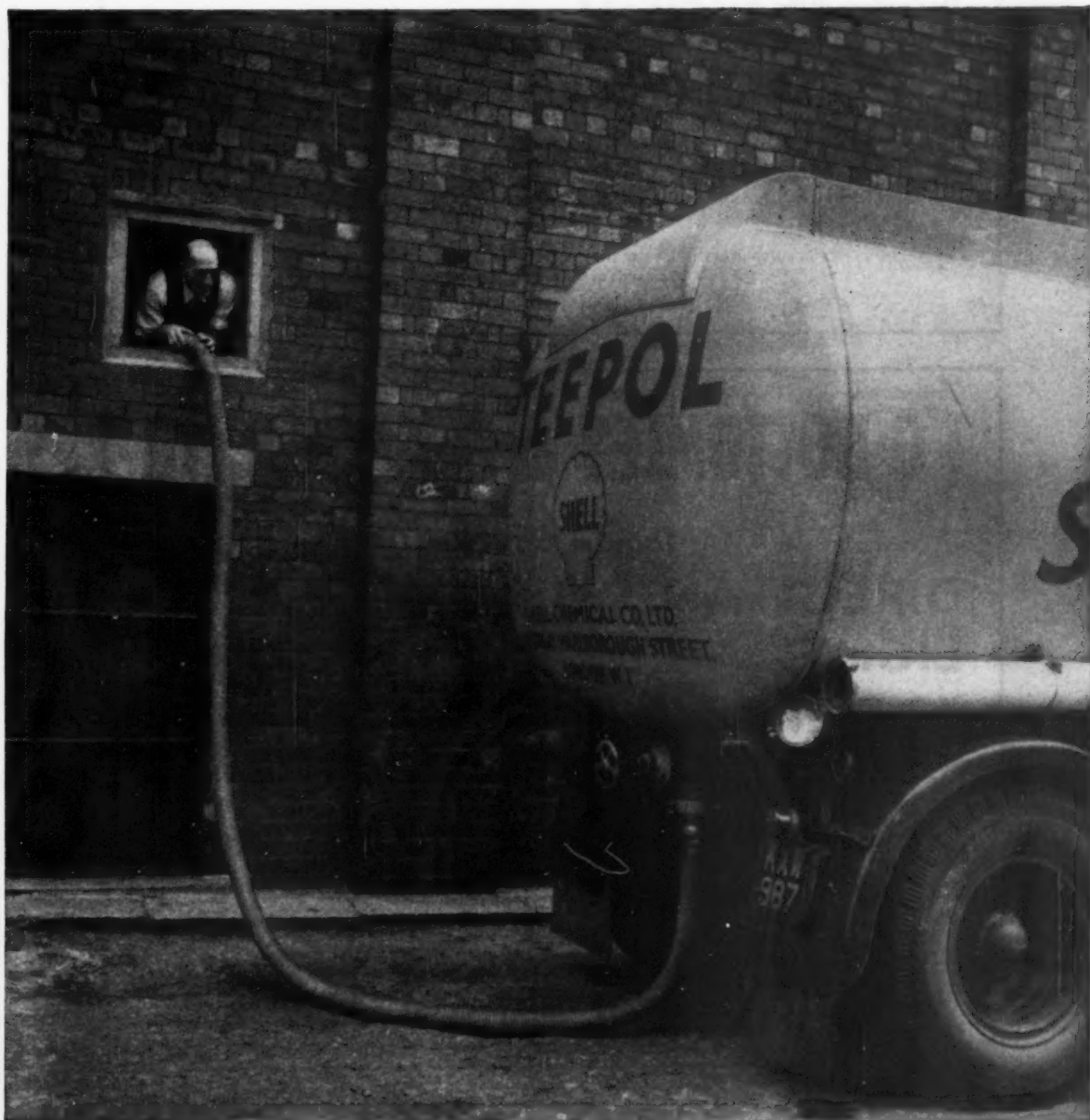
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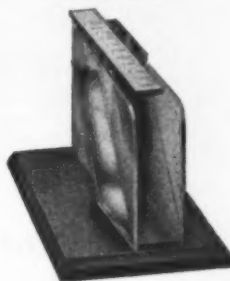
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Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1-10 of the January 1960 and pages 341-348 of the July 1959 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (Telephone Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

### Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

#### LECTURE

The Theory and Practice of Sodium Chlorite Bleaching

*J. K. Skelly*

#### COMMUNICATIONS

The Effect of Environment and Substituents on the Photochemical Activity  
of Anthraquinonoid Vat Dyes and the Role of  $n \rightarrow \pi^*$  Transitions

*N. K. Bridge*

Quinonoid Dyes. XIV—Relation between Coplanarity and Substantivity of Quinonoid  
Dyes applied to Secondary Cellulose Acetate and Cellulosic Fibres

*E. H. Daruwalla, S. S. Rao, and B. D. Tilak*

The English Contribution to the Development of Copper-plate Printing

*P. C. Floud*

The Chemistry of Esters of Leuco Vat Dyes

IV—Oxidation with Solutions of Nitrous Acid

*A. Johnson and A. P. Lockett*

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# THE JOURNAL

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Volume 76 Number 6

JUNE 1960

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### Proceedings of the Society

#### The Dyeing of Wool by Solvent-assisted Processes

W. BEAL, K. DICKINSON, and E. BELLHOUSE

*Meetings of the Midlands Section held at the King's Head, Loughborough, on 28th October 1959, Mr. A. S. Cluley in the chair; and of the Scottish Section held jointly with the Textile Institute at the Scottish Woollen Technical College, Galashiels, on 11th February 1960, Mr. E. Y. Johnston in the chair*

The influence of solvents, in particular benzyl alcohol, on the normal processes of wool dyeing and printing is reviewed in detail. The significance of the effect and the methods of utilising it are discussed. Consideration is given to the practical and commercial aspects of solvent-assisted techniques for dyeing and printing wool.

#### INTRODUCTION

When dyeing problems are mentioned, many people immediately think of the newer synthetic fibres or their blends and assume that natural fibres such as wool and cotton now present very few difficulties. Whilst it is true that a wide range of hues can be obtained on wool, it would be wrong to suppose that there are no remaining problems. Brighter colours and better fastness properties are constantly being required, and these present a problem to the dye manufacturer. There is also a demand for easier or quicker dyeing processes and for methods of dyeing which will leave the wool in a better condition than some conventional methods.

There is one outstanding difference between the methods of dyeing available for wool and cotton. Whilst cotton can be dyed by a variety of continuous processes, there are as yet no continuous dyeing methods for wool which are used to any appreciable extent in this country. Several methods have been suggested, the most recent being that described by Hirsbrunner<sup>1</sup>. This paper is not concerned with the continuous dyeing of wool, but with a field which is closely related to it, in that the principal advantage of the proposed method is that the condition of the material is preserved by using a relatively short time and temperatures much lower than those used in conventional dyeing. The method is based on the use of an organic solvent as a dyeing assistant.

It has been known for several years that the rate of absorption of dyes by wool is affected by the presence of an organic solvent. Peters and Stevens<sup>2,3</sup> showed that certain alcohols, phenols and amines, when added to an aqueous dyebath, markedly increased the rate of absorption. They also showed that very good exhaustion of the dyebath could be obtained in a relatively short time

and that this occurred at temperatures much lower than those normally used for the dyeing of wool, i.e. appreciably below the boil.

Similar results were obtained by Kärholm and Lindberg<sup>4,5</sup>, who examined the effect of the wool cuticle on the rate of sorption of dyes from baths containing alcoholic potassium hydroxide, n-butanol and amyl alcohol.

#### THEORETICAL ASPECTS

The underlying principle is the use of an organic solvent which is only sparingly soluble in water, but which is a very good solvent for the dye or pigment being used. This solvent should have affinity for the fibre, but its affinity for the dye should be less than that of the fibre. The aqueous phase of the dyebath will therefore act as a reservoir, dye being transferred continuously from the aqueous phase to the solvent phase and thus to the fibre, the organic chemical acting as an accelerator. It is therefore more appropriate to refer to the "solvent-assisted method of dyeing" than to "solvent dyeing", since the latter would imply a much higher proportion of dyeing assistant than is actually needed.

The results obtained by different workers have given rise to three theories concerning the mechanism involved. Alexander and Stacey<sup>6</sup> have suggested that the solvent acts as a hydrogen-bond breaker, thus preventing the formation of dye aggregates in solution, even at room temperature. Spectrophotometric measurements have indicated that the degree of aggregation is greatly reduced in an organic solvent or a solvent-water mixture, as compared with an aqueous solution at the same temperature. Furthermore, when a suitable solvent is added to a cold aqueous solution of an aggregated dye, e.g. Polar Brilliant Red BN conc. (C.I. Acid



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The results obtained by different workers have given rise to three theories concerning the mechanism involved. Alexander and Stacey<sup>6</sup> have suggested that the solvent acts as a hydrogen-bond breaker, thus preventing the formation of dye aggregates in solution, even at room temperature. Spectrophotometric measurements have indicated that the degree of aggregation is greatly reduced in an organic solvent or a solvent-water mixture, as compared with an aqueous solution at the same temperature. Furthermore, when a suitable solvent is added to a cold aqueous solution of an aggregated dye, e.g. Polar Brilliant Red BN conc. (C.I. Acid



Red 130), the colour of the solution becomes similar to that of an aqueous solution of the same dye at temperatures near the boil. This effect, by itself, is insufficient to account for the increased rate of dyeing, since some solvents, although they break down dye aggregates, do not accelerate dye absorption.

According to the second theory<sup>7</sup>, a layer of solvent is formed on the fibre surface, so in order to be a successful accelerator the solvent must have some affinity for the fibre. Since the dye is highly soluble in the solvent phase, its rate of diffusion into this phase, and thence into the fibre itself, is very rapid. Dyeing can therefore be carried out at much lower temperatures than those normally used with aqueous dyebaths, where high thermal energy is needed by the dye molecules to overcome the energy barrier of the wool-water interface.

Peters and Stevens<sup>8</sup> used a solvent-water bath for dyeing cellulosic fibres, the solvent (butanol) forming the bulk of the external phase. They observed that water was preferentially taken up by the cotton and promoted rapid transfer of highly anionic direct and other dyes from the external phase to the fibre. They considered that this represented the reverse state of affairs to that obtaining in the water-solvent dyebaths found to be effective for dyeing wool with essentially hydrophobic dyes.

The third theory<sup>9</sup> assumes that the solvent modifies the fibre in some way so as to facilitate the uptake of dye, as in the "carrier" method for dyeing synthetic fibres. According to this theory the solvent is absorbed by, and precedes the dye into, the fibre, where the internal bonds are ruptured or loosened, thus facilitating diffusion of the dye. It has also been suggested that the solvent acts by increasing the permeability of the wool cuticle, but our tests have shown no significant swelling of the fibre.

#### LABORATORY TRIALS

Whatever the mechanism, the phenomenon of solvent dyeing is real, and we believe that its practical implications could be of considerable importance. We therefore decided to find out whether it would form the basis of a commercially satisfactory method of dyeing.

#### Choice of Solvent

The first step was to examine a large number of organic chemicals which might be used. Initially we examined only compounds which—

- (1) Had little odour
- (2) Were non-toxic under the conditions of usage and would not give rise to dermatitis
- (3) Had low aqueous solubility
- (4) Were good solvents for most wool dyes
- (5) Had no adverse effect on the wool fibre
- (6) Presented no serious problems of effluent disposal.

Over 200 compounds have so far been examined, and for many purposes benzyl alcohol has been found to be most satisfactory. Most of the work discussed in this paper has therefore been carried

out using benzyl alcohol as the solvent or accelerator.

There is, however, one other possibility which should not be forgotten. Some compounds which are virtually insoluble in water would otherwise be suitable accelerators, and experiments employing the following two methods have been carried out with a view to utilising such compounds.

(a) The accelerator is emulsified in water. The emulsifying agent must not combine with the dye to any extent, thus interfering with its uptake or fastness properties. Lister<sup>10</sup> has suggested that the emulsifying agent should have high affinity for the fibre, since this would result in a higher concentration of the accelerator at the wool-water interface than in the aqueous phase and so make the process more economical.

(b) A second solvent is used in which the first solvent (or accelerator) is completely soluble and which is itself miscible with water in the proportions required, e.g. acetone is used as a solvent for toluene (the accelerator).

Although they complicate the system, these two alternatives may have advantages from the point of view of cost, in that with the first alternative a small amount of accelerator could be used and kept mainly where it is required, i.e. at the wool-water interface, whilst with the second, very cheap compounds can be used. It was soon found that, whilst there is usually a progressive increase in the rate of strike with increasing amounts of accelerator, there is an optimum amount for maximum exhaustion of the dyebath. Too much accelerator results in poor exhaustion of the dyebath.

After examining these alternative methods for some time, however, we reverted to the use of accelerators which are soluble in water at the required concentrations.

#### Choice of Dyes

The second point to be decided was the type of colouring matter to be used. Dyes of high solvent-solubility and low water-solubility were likely to be the most useful, provided that they had sufficient affinity for the fibre.

Peters and Stevens<sup>2</sup> have described a partition-ratio test which gives a quick guide to the solubility of dyes. To an aqueous solution of the dye is added an approximately equal amount of benzyl alcohol. The mixture is then shaken, at the appropriate temperature, and the two liquids allowed to separate. If acid is to be used in the dyeing, a repeat test is made in the presence of the appropriate amount of acid. We have classified most of the Geigy wool dyes by this method, using the following 1-10 scale based on visual assessment—

- 1 = No dye in solvent phase
- 5 = Equal amounts of dye in the two phases
- 10 = All dye in solvent phase

It has since been found that this method is not entirely reliable: some dyes, with a rating of only 3, nevertheless give a satisfactory dyeing by the solvent-assisted method. The most important factor seems to be the rate at which dye transfers from the aqueous to the solvent phase. However,



if a dye has a rating of 1, e.g. Wool Blue RL (C.I. Acid Blue 92), it will not dye by this method, unless the conditions are modified. For example, three comparative dyeings of Wool Blue RL were made with—

- (1) An acidified aqueous solution
- (2) An acidified aqueous solution containing benzyl alcohol
- (3) A dyebath similar to (2), but containing a suitable cationic compound, e.g. cetyltrimethylammonium bromide.

Dyeings (1) and (2) were similar, but (3) showed a much more rapid strike, probably due to the cationic compound combining with the dye and effectively reducing its anionic character and its aqueous solubility. A similar result is obtained with reactive dyes.

Neutral-dyeing metal-complex dyes of the Irgalan type are obviously very suitable for solvent-assisted dyeing, since they have very good solubility in solvents such as benzyl alcohol, whilst their rating in the partition test is 9 or 10 in all cases owing to their similarity in chemical constitution.

Acid dyes, on the other hand, vary widely in their suitability for the process, but there are sufficient suitable dyes to give a wide range of colours.

Many chrome dyes may also be applied by this method, although we have not yet found any satisfactory means of accelerating the afterchrome stage. However, an appreciable number of dyes can be developed satisfactorily by chroming for 30 min. at 80–100°C., one example being Eriochrome Black PV (C.I. Mordant Black 9).

Peters and Stevens<sup>2</sup> raised the question of using suitable pigments, e.g. Irgacet Scarlet RL, for the coloration of wool. We have carried out similar experiments, but have not yet succeeded in developing a process which could be used commercially. Nevertheless, the idea is very attractive, since very good fastness to wet treatments such as scouring, potting and cross-dyeing would be expected if water-insoluble colouring matters could be applied satisfactorily.

#### Methods of Application

Consideration was next given to the application of the solvent-assisted process to various dyeing systems, and it was decided that the following were the most promising—

- (1) Continuous dyeing systems
- (2) Padding and development
- (3) Printing
- (4) Batch dyeing of loose stock or slubbing.

Since (1) and (2) have been discussed recently by Hirsbrunner<sup>1</sup>, this paper is confined mainly to (4), with some reference to (3).

In any dyeing it is desirable to obtain level results. Our first laboratory trials were therefore directed towards attaining levelness, whilst ensuring that the colour of the dyeing was fully developed and had the normal fastness properties.

Before a dyeing was passed as satisfactory, the following tests were made—

A conventional dyeing was carried out at the boil, using the same recipe and the same material as were used in the solvent-assisted dyeing. The solvent-dyed material was halved and one portion was "developed" at the boil for 30 min. in a blank bath containing only sufficient acid to ensure a minimum amount of bleeding into the liquor.

The dyeings were dried below 76°C., examined and compared for shade, strength and general appearance, fastness to washing (S.D.C. Wash Test No. 2, or Mechanical Wash Test A, depending on the dye used), light fastness, rubbing, and perspiration. It was found later that the tests for fastness to light, rubbing, and perspiration were usually unnecessary.

#### Yellowing

When the solvent-dyed material was treated at the boil for 30 min. in a blank acidified dyebath, the shade became slightly yellower and then corresponded quite closely to that of the conventional dyeing. Possible causes of the change in colour were thought to be—

- (i) Yellowing of the material in the 30-min. development at the boil
- (ii) Development of residual unfixed dye on the fibre
- (iii) Elimination of initial skitteriness
- (iv) A change in the colour of the dye itself on boiling under acid conditions.

Item (iv) was eliminated as a possible cause by comparing the spectrophotometric curves of a 0.053 g./litre solution of Irgalan Grey BL in butanol (a) before and (b) after boiling for 2 hr. under the acid conditions. The curves were found to be identical. Secondly, (ii) could not be the cause, since the loose dye would have been removed by a scouring process, which was not the case. It was thought that (iii) was not responsible, since the initial dyeing did not appear skittery, neither did the depth increase appreciably on boiling. It was found, however, that if the material was boiled for 30 min. before dyeing by the solvent technique, the colour subsequently obtained corresponded very closely to that of the conventional dyeing, and a further 30-min. boil then had little effect.

#### Influence of Different Factors

Fig. 1 illustrates the results obtained when wool flannel was dyed with 2.0% Irgalan Grey BL (C.I. Acid Black 58) at 60°C. for 30 min. with a liquor ratio of 40:1 in a Marney machine. It enables a comparison to be made between the effect of solvent concentration and the effect of pH. These experiments quickly showed that, for a given time, temperature, dye and fibre, the effect of solvent concentration is predominant, since it determines whether the dyeing will be completely developed in shade and fastness properties. The pH merely determines the rate of dyeing and final exhaustion obtained under the fixed conditions of time and temperature.

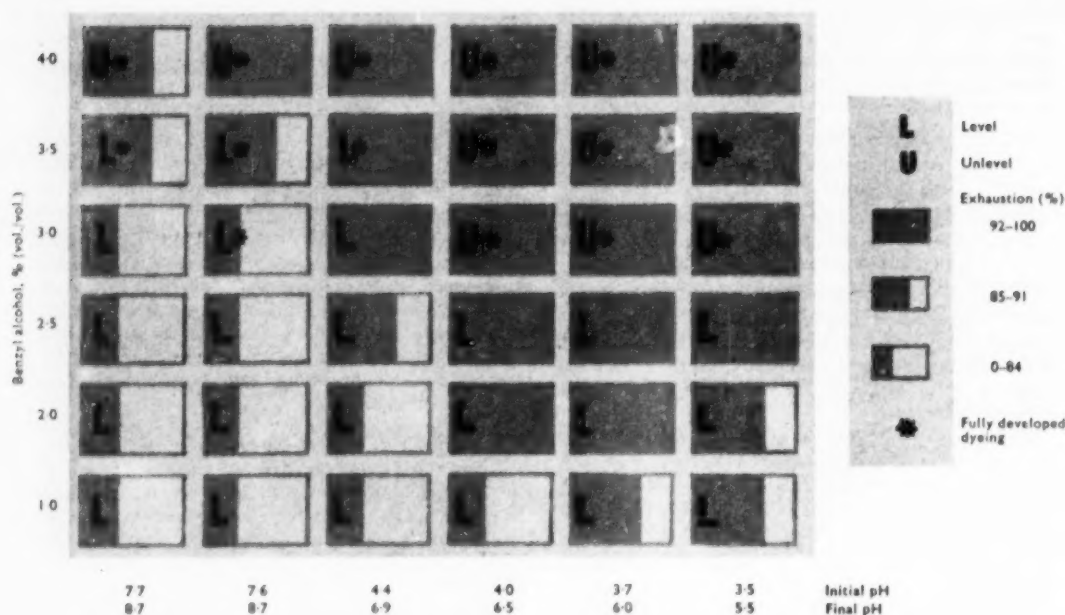


FIG. 1—Effect of Percentage Benzyl Alcohol and pH on Levelness and Exhaustion (2.0% Irgalan Grey BL at 60°C. in 40 vol.)

It was decided to investigate each factor individually, and for this purpose the following materials and conditions were employed—

Material	64s wool slubbing in oil (ca. 3% Class A combing oil)
Dye	2.0% Irgalan Grey BL
Benzyl alcohol	3.0% (vol./vol.)
Water	Bradford tap water (ca. 4° hardness)
Acid	1% acetic acid (40%)
pH	7.3
Temperature	70°C.
Liquor ratio	50:1

Each factor was varied while the others remained constant. The results of these experiments are illustrated in Fig. 2-8.

It is seen that concentration of benzyl alcohol and pH have a considerable effect on the rate of strike and final exhaustion (Fig. 2 and 3). Fig. 4 shows that temperature may be used to control the rate of strike, but that it has less effect than in a conventional dyeing. Under the conditions established, equilibrium is reached in ca. 60 min. (Fig. 5). Fig. 6 shows that, under otherwise identical conditions, dyeing is more

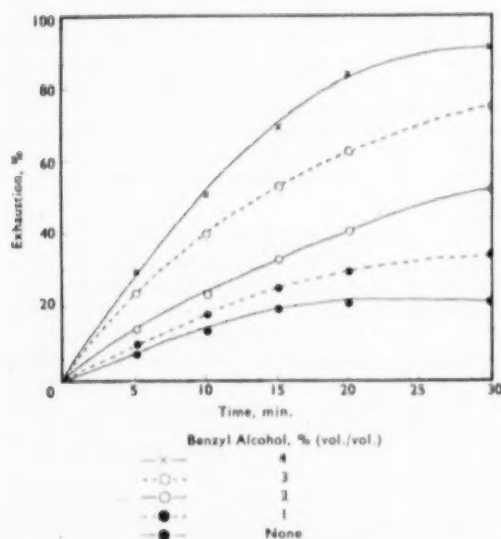


FIG. 2—Effect of Benzyl Alcohol Concentration (2.0% Irgalan Grey BL, 50:1 liquor ratio, 70°C., pH 7.3 using 1% acetic acid (40%))

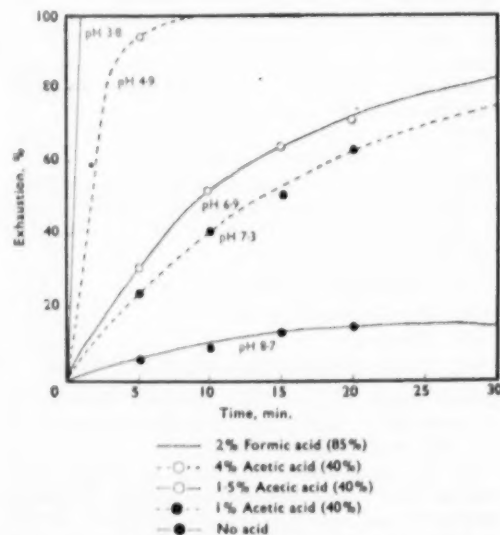


FIG. 3—Effect of pH (2% Irgalan Grey BL, 3% benzyl alcohol (vol./vol.), 50:1 liquor ratio, 70°C.)

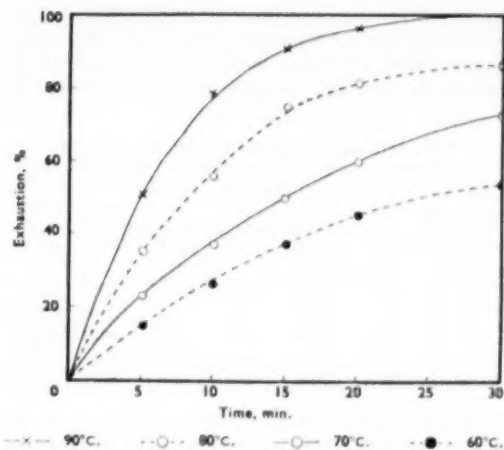


FIG. 4—Effect of Temperature (2% Irgalan Grey BL, 3% benzyl alcohol (vol./vol.), 50:1 liquor ratio, pH 7.3 using 1% acetic acid (40%))

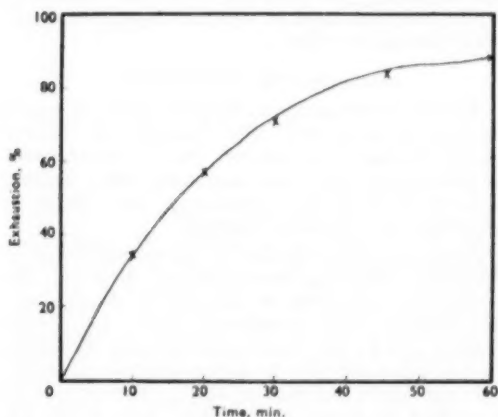


FIG. 5—Effect of Dyeing Time (2.0% Irgalan Grey BL, 3% benzyl alcohol (vol./vol.), 50:1 liquor ratio, 70°C, pH 7.3 using 1% acetic acid (40%))

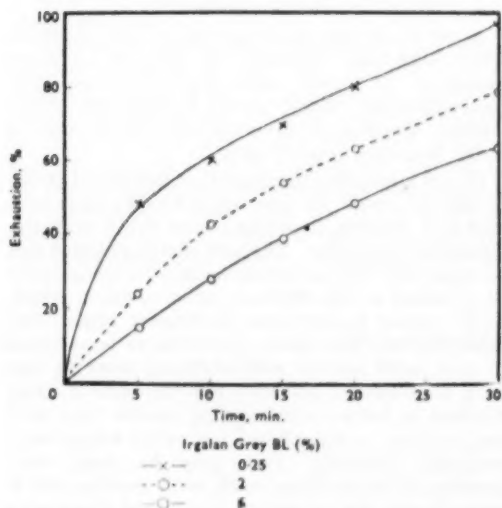


FIG. 6—Effect of Dye Concentration (3% benzyl alcohol (vol./vol.), 50:1 liquor ratio, 70°C, pH 7.3 using 1% acetic acid (40%))

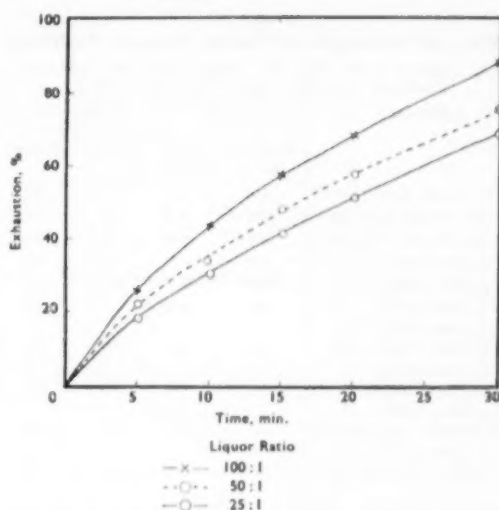


FIG. 7—Effect of Liquor:Goods Ratio (2% Irgalan Grey BL, 3% benzyl alcohol (vol./vol.), 70°C, pH 7.3 using 1% acetic acid (40%))

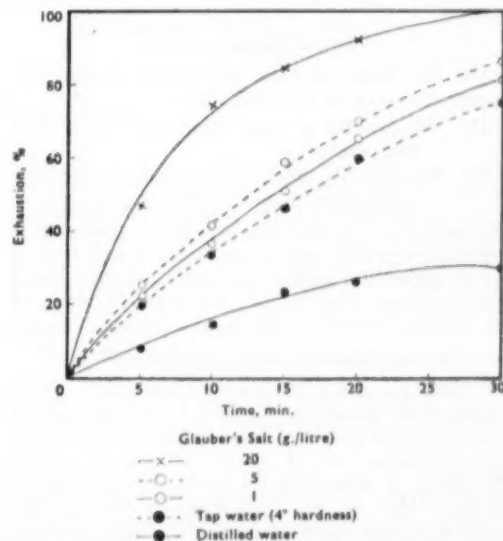


FIG. 8—Effect of Electrolyte Content at pH 7.3 (2% Irgalan Grey BL, 3% benzyl alcohol (vol./vol.), 50:1 liquor ratio, 70°C)

rapid in pale depths than in full depths, as would be expected. As the liquor ratio increases, the rate of exhaustion increases slightly (Fig. 7).

Fig. 8 shows that increasing the quantity of Glauber's salt increases the rate of exhaustion appreciably. This is very interesting, in view of the small effect which similar concentrations of Glauber's salt have on the rate of strike of this dye under normal dyeing conditions. Even very small amounts of electrolyte have a marked effect, as is seen (Fig. 8) when distilled water and Bradford tap water are compared.

Table I shows the effect of other electrolytes and of metal-chelating (sequestering) agents. More work is required in this connection, since the results cannot readily be explained by the effect of

TABLE I  
Effect on Exhaustion of Various Dyebath Additions  
(2% Irgalan Grey BL, 3% benzyl alcohol (vol./vol.),  
Bradford tap water, liquor ratio 50:1, 70°C.)

Addition	pH		Exhaustion (%) after—	
	Without Wool	With Wool	5 min.	15 min.
1% Acetic acid (40%)	4.0	7.0	25	55
1.5% Acetic acid (40%)	3.7	6.4	42	80
2.0% Acetic acid (40%)	3.6	5.6	60	95
1 g./litre NaCl	4.0	7.0	42.5	85
1 g./litre MgSO <sub>4</sub>	4.2	6.7	50	98
1 g./litre CaCl <sub>2</sub>	4.1	6.4	70	100
1 g./litre CaCl <sub>2</sub>	—	—	—	—
2 g./litre Irgalan BT	4.6	6.5	70	95
1 g./litre CaCl <sub>2</sub>	—	—	—	—
2 g./litre Calgon	—	5.6	75	100
1 g./litre CaCl <sub>2</sub>	—	—	—	—
10 g./litre Irgalan BT	—	6.6	17	30
0.1 g./litre CaCl <sub>2</sub>	—	—	—	—
1 g./litre Irgalan BT	—	6.9	17	30

the electrolyte on the rate of partition of the dye between the aqueous and solvent phases, unless it is assumed that metal salts of the dyes are being formed.

#### Choice of Dyeing Method

On the basis of this preliminary work, two approaches seemed possible, viz.—

- (1) To dye for a very short time at a high temperature
- (2) To dye at a relatively low temperature for a moderate length of time, e.g. 30 min.

Method (1) implies continuous dyeing, since this is virtually the only way of obtaining a satisfactory works procedure and level results in very short dyeing times. Method (2), with dyeing times of ca. 30 min., is suitable for routine batch dyeing.

#### COMMERCIAL CONSIDERATIONS

It was impossible in this investigation to ignore commercial considerations, so a study was made of the cost of the proposed method and, in particular, the additional cost of the accelerator or solvent. The latter is dependent on (a) the temperature of dyeing, and (b) the liquor:goods ratio. This ratio is almost constant for a particular machine, and since it was intended to use normal plant, it was evident that, for loose wool and slubbing dyeing, the ratio would lie between 10:1 and 20:1.

The amounts of benzyl alcohol needed are approximately 4% (vol./vol.) at 60°, 3% at 70°, and 2% at 80°C. Since benzyl alcohol costs about 3s. per lb., the cost of solvent per dyeing could be calculated. It varied between 7.25d. and 2s. 5d. per lb. of wool, and was obviously too high. We concluded that, if the process was to be of interest to the dyer, this cost would have to be reduced to 3–4d. per lb., so we turned our attention to the re-use of dye liquors. This was found to be possible, since the method gives very good exhaustion of the dye. Whether the amount of solvent lost is excessive depends on the volume of dye liquor removed with the wool, and to some extent on the dyeing conditions; but with a liquor:goods ratio of between 10:1 and 20:1 and a temperature of

60–80°C., the amount lost is ca. 12–20%. The estimated cost of repeated dyeings in the same liquor, after adding sufficient benzyl alcohol to restore the original strength, is given in Table II.

TABLE II  
Cost of Benzyl Alcohol per lb. Wool Dyed  
(pence per lb., calc. for benzyl alcohol at 3s. per lb.)

No. of Dyeings in the same Liquor	Temperature (°C.)					
	Liquor: Goods Ratio					
	10:1	20:1	10:1	20:1	30:1	40:1
1	12.5	25.0	7.25	14.5	21.75	29.0
2	10.0	16.2	4.8	8.3	12.0	15.5
3	9.0	13.3	4.0	6.1	8.6	11.0
4	8.3	11.6	3.5	5.2	7.1	9.0
5	7.6	10.8	3.2	4.8	6.1	7.6

It is seen that dyeing at 60°C. is unlikely to be acceptable unless cheaper or more efficient solvents can be found. At 80°C., however, we are able to achieve our aim of 4d. per lb. by using the same dye liquor five times. In practice, the same dye liquor has been used as many as seventeen times with satisfactory results.

#### EXPERIMENTAL DIFFICULTIES

We have been unable to devise a simple means of measuring accurately the amount of benzyl alcohol in aqueous solution. Spectrophotometric measurements have been suggested, but a simpler method is desirable—preferably one which is applicable to coloured solutions.

A second problem is that of measuring the pH of dyebaths containing benzyl alcohol. Marcou<sup>11</sup> has shown that indicators are affected by the presence of surface-active compounds such as benzyl alcohol, and we have found that the glass electrodes used in pH meters can be adversely affected, so the readings given are not reliable. However, some combined electrodes are suitable. Most of the pH values recorded in this paper refer to "blank" baths, i.e. to dyebaths without benzyl alcohol.

#### BULK TRIALS

Some 40–50 bulk trials have so far been made on loose wool and slubbing, as well as on loose cashmere. In general, these trials have been very successful, and many useful lessons have been learned. Several requirements have to be met in order to obtain level results.

(1) It is essential to ensure that the rate of strike of the dye under the prevailing conditions is such that it is possible to obtain a level result with the circulation available. The rate of strike (which can be unusually high in solvent-assisted dyeing) must be adjusted to the efficiency of circulation, which varies widely in machines of different types. For example, very high rates of strike have been found to give level results with slubbing dyed in top form on a spindle machine, but the same method resulted in failure when dyeing similar tops in a can machine, unless the rate of strike was greatly reduced. Similarly, yarn may be dyed very quickly in cheese form with level results, but a much slower dyeing process is required on yarn in hank form.

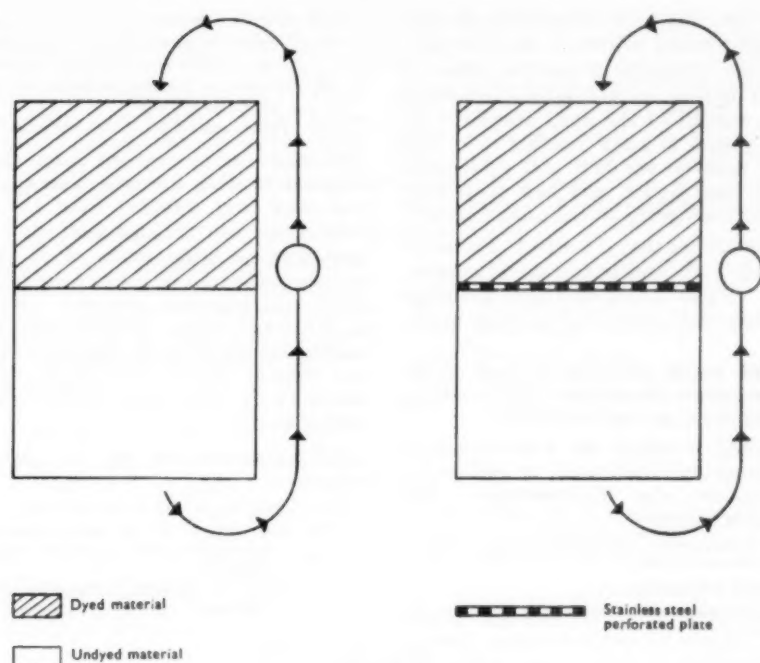


Fig. 9—Apparatus for Migration Test

(2) It is preferable to establish a uniform pH throughout the material to be dyed *before* commencing dyeing by the solvent method<sup>12</sup>, because the rate of strike is usually high, and non-uniform pH causes unlevel dyeings. It is not always easy to establish a uniform pH in bulk practice; it is especially difficult where circulation is poor and a pH near 7 is required on material which was previously markedly alkaline. It is easier to establish a lower pH uniformly, but when, as is often the case, dyeing has to be carried out near pH 7, e.g. on a top initially at pH 9–10, the use of a buffer is advantageous, unless the circulation is really efficient.

Loose wool and slubbing are often dyed without further additions of dye, but if extra dye is required, it must be added systematically. Furthermore, if several dyeings are to be made in the same liquor, it is advisable to control the initial strike so that dyeing may safely be started and finished at the same temperature, when shading additions can be made easily. Under ideal conditions a dyeing requires 30–45 min., but a shading addition should be fixed in 15–30 min., depending upon the

amount of dye added. In practice we have obtained level results under conditions where unlevel results would be expected from conventional dyeings using the same dye with a similar rate of strike. Several factors may be involved: the initial strike obtained is more even under these conditions than in the absence of the solvent, and there is increased migration.

This additional migration takes place largely on the surface of the fibres and not through the aqueous phase. If dyed slubbing is packed into a holder together with undyed slubbing and the dye liquor circulated as illustrated in Fig. 9, the migration can be measured under standard conditions of time, temperature, etc. With a blank dyebath it was found that migration was appreciably greater when benzyl alcohol was present, irrespective of whether the material had been dyed originally by the solvent-assisted or the conventional method. When the dyed slubbing was separated from the undyed by a stainless steel perforated plate, or a layer of glass wool, and the experiment repeated, it was found that the presence of solvent had little effect, and the

TABLE III  
Oil Content of Solvent-dyed Slubbing

Wool Slubbing	No. of Solvent-assisted Dyeings	Dye	Assistant	Undyed	Oil Content (%)	
					Conventional Dyeing	Solvent-assisted Dyeings
64s	7	Irgalan combination	Ammonium sulphate	3.5	3.9	3.1–3.9
64s	3	Irgalan combination	Ammonium sulphate	3.5	3.9	3.2–3.6
64s	8	Eriochrome Black T	Acetic acid	3.8	3.7	4.4–4.7
56s	2	Polar Brilliant Blue RAW	Acetic acid	2.4	2.5	2.6–2.7



migration was very similar to that obtained with the blank liquor without solvent in the first test.

A further point investigated was the effect of solvent-assisted dyeing on the ether-extractable oil and grease content of the dyed material. In particular, we wished to know whether there was any difference between the first and subsequent dyeings in the same liquor, and how they compared with a normal dyeing on the same material.

Table III shows that the oil content of solvent-dyed slubbing is very similar to that of conventional dyeings. There is also very little difference between the first and subsequent dyeings in the same liquor.

A final point worth recording is that moth-proofing can be carried out satisfactorily by adding Mitin FF to a solvent-assisted dyebath.

Before deciding to adopt the solvent-assisted process, the wool dyer will wish to weigh the advantages against the disadvantages. The advantages are as follows—

- (1) Quick dyeing, with consequent saving in labour and overhead costs
- (2) Increased production
- (3) Saving of steam and, therefore, lower fuel costs

- (4) Saving of water
- (5) Slightly brighter colours, because the wool does not yellow as much as in normal dyeing
- (6) Suitability for use in many currently available dyeing machines
- (7) Better condition of the material<sup>15</sup>.

In order to substantiate claim (7), large-scale comparative trials are being carried out on both loose wool and slubbing dyed by the solvent-assisted and conventional methods. An accurate assessment is being made of the carding and spinning properties of the loose-wool dyeings, and of the combing, etc., properties of the slubbing. So far, the results indicate that the solvent-assisted method gives an appreciable improvement over normal dyeing procedures: the saving in noilage or fly alone could easily be a major controlling factor.

The disadvantages of the process are as follows—

- (1) Additional cost of the solvent
- (2) Necessity of having a suitable dyeing machine, preferably with a reserve tank of adequate capacity
- (3) Need for planning production so as to ensure the best re-use of dye liquors.

TABLE IV  
Tests on Wool Printed with 2.0% Polar Brilliant Violet BL

TYPICAL PASTE						
2	Dye					
42	Water					
41	Solvitose H4M (8:1)					
3	Formic acid (85%)					
12	Benzyl alcohol					
—						
100						
Benzyl Alcohol (%)	Steaming Time (min.)	Depth of Colour	Haloing	Fastness S.D.C.	Wash Test No. 2	
0	0	1*	1*	1	5	5
0	2.5	3	2	2	5	5
0	5	3-4	4	2	5	5
0	10	3-4	4	3	5	5
0	20	3-4	4	4	5	5
3	0	1	1	1	5	5
3	2.5	3-4	2	3	5	5
3	5	3-4	2	3	5	5
3	10	4	2	3	5	5
3	20	4	2	4	5	5
6	0	3	2	1	5	5
6	2.5	4-5	2	3-4	5	5
6	5	4-5	2	3-4	5	5
6	10	4-5	2	3-4	5	5
6	20	5	2	4	5	5
9	0	5	3	3	5	5
9	2.5	5	4	4	5	5
9	5	5	4	4	5	5
9	10	5	4	5	5	5
9	20	5	4	5	5	5
12	0	5	5	3	5	5
12	2.5	5	5	4	5	5
12	5	5	5	4	5	5
12	10	5	5	5	5	5
12	20	5	5	5	5	5

\* Very poor

For some expensive fibres, e.g. cashmere, the cost of the solvent is far outweighed by the advantages of the process. On other animal fibres the advantages and disadvantages are more evenly balanced, but several firms are examining the process. Patents covering this field have been applied for, and the process has been provisionally named the "Irga-Solvent process for wool dyeing".

#### PRINTING

It is possible to improve wool printing processes by using an accelerator of the benzyl alcohol type in the printing paste. Delmenico<sup>14</sup> has given details about its use in mélange printing, and we have investigated this aspect, as well as the screen and roller printing of wool.

#### Mélange Printing

In mélange printing, the normal steaming time can be cut by at least 50% by adding 6–12 parts of benzyl alcohol per 100 parts of paste. The resulting advantages are—

- (1) Higher throughput in the steaming plant
- (2) Less yellowing of the unprinted portions
- (3) Better condition of the final material
- (4) Less colour bleed in backwashing
- (5) Apparently better yield (this may be due to the excellent wetting properties of benzyl alcohol allowing greater uptake of paste).

When using benzyl alcohol, it is possible to omit the urea and wetting agents normally used in the paste, thus partially offsetting the extra cost of the benzyl alcohol.

#### Fabric Printing

It was next decided to determine whether the solvent-assisted technique offered any advantages over conventional methods of printing wool fabrics.

Except in the exclusive fashion houses, printed wool fabric has never been freely available in this country in any quantity. It is usually considered necessary to chlorinate the material in order to obtain sufficient uptake of dye, and it is not easy to chlorinate wool cloth uniformly. Laboratory experiments using pastes containing selected dyes and benzyl alcohol have shown that chlorination could be omitted. If the cloth had been chlorinated to confer shrink-resistance, the addition of benzyl alcohol minimised differences in shade arising from uneven treatment. Steaming and washing-off times could be reduced considerably.

Polar Brilliant Violet BL is suitable for this process, and Table V shows the results obtained with this dye on chlorinated wool flannel, in experiments to determine (a) the steaming time

required, and (b) the percentage of benzyl alcohol required in the paste. Under ideal laboratory conditions, it appears that steaming for 20–30 min. at atmospheric pressure is sufficient when using 12% benzyl alcohol in the paste.

On the basis of many similar trials, as well as bulk tests, the following conclusions have been reached with regard to the advantages and disadvantages of incorporating benzyl alcohol in the print paste—

#### ADVANTAGES

- (1) Better colour value
- (2) Much shorter steaming time
- (3) Much shorter washing-off time
- (4) Better wet fastness
- (5) Materials which are inclined to roll, e.g. knitted fabrics, can be printed, because the prints do not mark off in washing or drying.

#### DISADVANTAGES

- (1) Benzyl alcohol attacks most types of screen lacquer
- (2) Benzyl alcohol pastes stain silk or nylon (but not Terylene) screens
- (3) Slight additional cost.

#### CONCLUSIONS

There are many possible outlets for the solvent-assisted method of fibre coloration. In any particular field, much work is required in order to develop a process which can be used commercially, but recommendations have now been made for dyeing animal fibres, especially in the form of loose stock or slubbing.

\* \* \*

We wish to express our thanks to Dr. C. B. Stevens for his criticism and advice, and to the Geigy Company Ltd. for permission to publish this paper.

THE GEIGY COMPANY LTD.

RHODES

MIDDLETON

MANCHESTER

(MS. received 23rd November 1959)

#### References

- <sup>1</sup> Hirsbrunner, I.F.A.T.C.C. Congress, London (Sept 1959).
- <sup>2</sup> Peters and Stevens, *Dyer*, **115**, 327 (1956).
- <sup>3</sup> Idem, *J.S.D.C.*, **72**, 100 (1956).
- <sup>4</sup> Lindberg, *Text. Research J.*, **23**, 573 (1953).
- <sup>5</sup> Kärholm and Lindberg, *ibid.*, **26**, 528 (1956).
- <sup>6</sup> Alexander and Stacey, *J.S.D.C.*, **72**, 241 (1956).
- <sup>7</sup> Peters and Stevens, *ibid.*, **37**, 23 (1957).
- <sup>8</sup> Idem, *ibid.*, **74**, 183 (1958).
- <sup>9</sup> A.A.T.C.C., Delaware Valley Section, *Amer. Dyestuff Rep.*, **47**, 789 (1958).
- <sup>10</sup> Lister, *Textil-Rund.*, **11**, 463 (1956).
- <sup>11</sup> Marrou, *ibid.*, **9**, 128 (1954).
- <sup>12</sup> Noble, *J.S.D.C.*, **61**, 328 (1945).
- <sup>13</sup> Gulbrandson, *Text. Research J.*, **28**, 965 (1958).
- <sup>14</sup> Delmenico, *ibid.*, **27**, 809 (1957).

## COMMUNICATIONS

# The Radiation-induced Graft Copolymerisation of Methacrylic Acid to Nylon

R. ROBERTS and J. K. THOMAS

The grafting of methacrylic acid to 6,6-nylon has been achieved by using the  $\gamma$ -radiation from a  $^{60}\text{Co}$   $\gamma$ -source. The effect of total radiation dosage and temperature on the rate of grafting is reported, and interpreted using current copolymerisation concepts. The effect of the new surface on the solubility of the nylon in various solvents, and on the surface electrical resistance, is also described and discussed briefly.

## INTRODUCTION

Over the past few years the literature on radiation chemistry has contained an increasing amount of work on the radiation-induced grafting of monomers to various polymers<sup>1-12</sup>. Four main methods have been used, viz.—

- (1) Simultaneous Grafting
  - (a) Film irradiated while immersed in monomer
  - (b) Film irradiated while swollen in monomer
- (2) Post-irradiation Effect
  - (a) Irradiation of dry film, fibre or fabric *in vacuo*, followed by addition of monomer
  - (b) Irradiation of dry material in air, followed by addition of monomer.

Methods 1(a) and 1(b) suffer from the disadvantage that amounts of homopolymer are formed which depend on the radiation-sensitivity of the monomer. It is possible for this homopolymerisation to be quite large and of the order of the grafting reaction or larger. However, the amount of homopolymerisation in methods 2(a) and 2(b) is quite small compared with the amount of grafting. In method 2(a) trapped radical sites are formed on the polymer which can promote polymerisation of a suitable monomer, and in method 2(b) peroxides and/or hydroperoxides are formed which can be decomposed on heating, thereby promoting polymerisation, as in the normal peroxide-induced polymerisation method.

In the present work, the effect on the electrical properties of nylon of small amounts of grafted methacrylic acid was investigated. Usually amounts not exceeding 10% by weight of methacrylic acid were grafted on to 6,6-nylon and the modification of the electrical properties, as shown by the electrical resistance of the nylon, was measured.

## EXPERIMENTAL

## Materials

6,6-Nylon fibre and fabric were obtained from British Nylon Spinners Ltd. The methacrylic acid, which contained 0.1% hydroquinone as a stabiliser, was distilled twice *in vacuo* before use. All other reagents were AnalaR grade.

## Irradiation Technique and Grafting Procedure

The nylon fabric or fibre was irradiated in air by  $\gamma$ -rays from a 120-curie  $^{60}\text{Co}$  source, at a dose rate

of  $10^5$  rads/hr.\*. In a typical experiment 0.2 g. of irradiated nylon was covered by 4 ml. of a 0.23 M. aqueous monomer solution in an acetate buffer at pH 3.7, in a 10-ml. glass bulb. The solution was attached to a vacuum line and deaerated by the usual procedure of pumping off the cleared space, followed by shaking of the solution in a vibro-shaker. This procedure was repeated three times. Deaerating the nylon and the solution separately, followed by pouring the solution under vacuum on to the nylon, gave the same results as the first procedure. The reaction mixture was placed under vacuum, in a thermostat bath at a chosen temperature for a suitable length of time.

At the end of this time the vessel was removed, cooled in cold water and broken open. One ml. was suitably diluted in 0.01 N. sulphuric acid and the optical density at 210 m $\mu$ , measured on a Hilger ultraviolet spectrophotometer; from this the double-bond [C=C] concentration was calculated, suitable calibrations having already been made and a molar extinction coefficient of 8,500 obtained from the absorption of the double bond in methacrylic acid at this wavelength.

A sample of each of the remaining solutions was titrated potentiometrically with 0.01 N. sodium hydroxide to determine the total [H<sup>+</sup>] of the solution, after correcting for the acetic acid in the buffer. This total [H<sup>+</sup>] was a measure of the methacrylic acid remaining and the homopolymer formed, so the decrease in total [H<sup>+</sup>] then gave the amount of methacrylic acid grafted to the nylon, and the decrease in double-bond concentration the amount grafted and the amount of homopolymer formed.

The grafted nylon was refluxed with three lots of 100 ml. methanol, for three 1-hr. periods, dried under vacuum and kept for subsequent investigation.

## RESULTS

Fig. 1 illustrates the amounts of graft copolymer and homopolymer formed per 0.2 g. of nylon irradiated to a dose of 0.3 megarad in air. It is seen that the rate of homopolymerisation is much smaller than the rate of the grafting reaction. This, as has already been explained, is in accordance with the formation of organic peroxides and hydroperoxides on the fibre, the subsequent decomposition of which initiates the polymerisation of the methacrylic acid.

\* 1 rad = 100 ergs of energy absorbed per g. of substance.

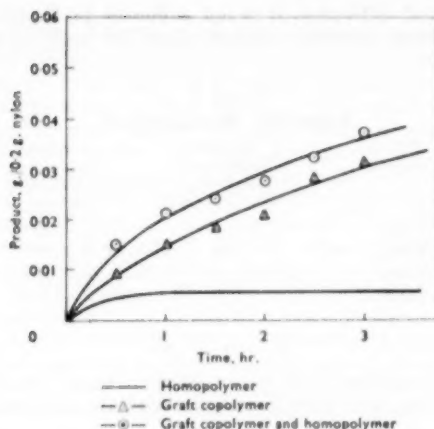


FIG. 1—Effect of Time on Production of Graft Copolymer and Homopolymer at 75°C. (dose to nylon 0.3 Mrad in air)

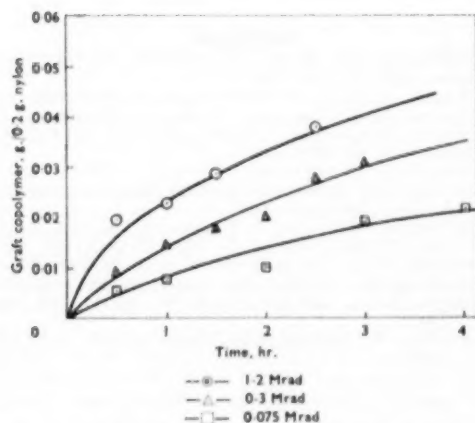


FIG. 2—Effect of Dosage on Production of Graft Copolymer

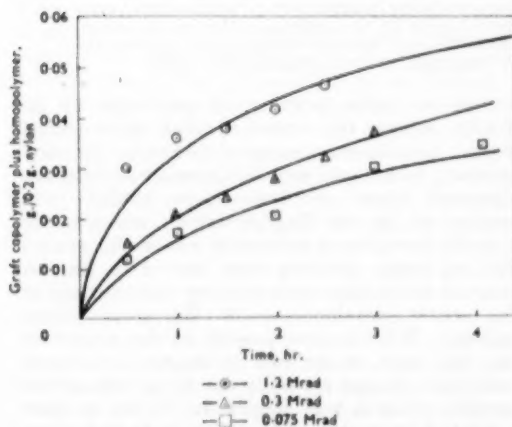


FIG. 3—Effect of Dosage on Production of Graft Copolymer plus Homopolymer

In Fig. 2 and 3 the effect of total dose on the rate of grafting and homopolymerisation is shown. There appears to be no simple relationship connecting the reaction rate and the total dose. The only conclusion that is drawn is that increase in the total dose leads to an increase in the grafting and homopolymerisation rates. This occurs as a natural consequence of the fact that increase in total dose could lead to an increase in the peroxidic content of the irradiated nylon.

A further insight into the polymerising process is provided by the effect of temperature on the rates of grafting to a nylon fibre which had been irradiated to a total dose of 0.3 megarad. Inspection of Fig. 4 reveals that the rates of grafting and homopolymerisation at 75°C. are  $2.9 \pm 0.2$  times as great as those at 55°C., giving an activation energy of  $13 \pm 1$  kcal./mole for the whole process.

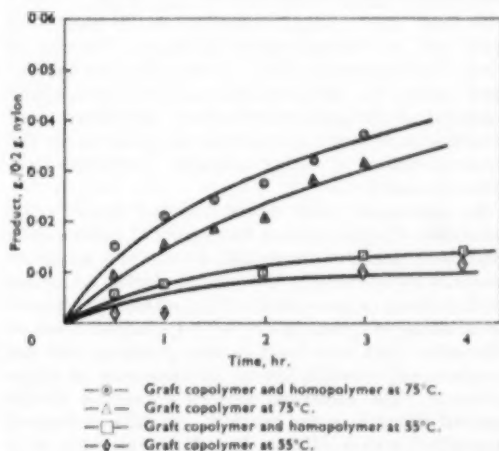


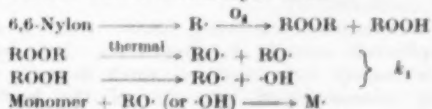
FIG. 4—Effect of Temperature on Production of Graft Copolymer and Homopolymer

In all the above experiments a correction was made for a small amount of thermal polymerisation which was not caused by the irradiation-produced peroxides. Since the amount was usually quite low, suitable corrections could easily be made.

#### DISCUSSION

Chapiro<sup>4</sup> has shown that peroxide cross-links and/or hydroperoxides are formed when polyethylene is irradiated in the presence of oxygen. He also showed that the peroxides and hydroperoxides could be thermally decomposed at elevated temperatures in the presence of vinyl monomers to produce graft copolymers.

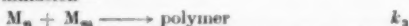
The present work can also be explained on this basis, irradiation of the nylon producing an organic peroxide ROOR, or hydroperoxide ROOH, which decomposes thermally, producing free radicals which are able to initiate the polymerisation of the methacrylic acid—



Propagation—



Termination—



From this it can be shown that the rate of disappearance of monomer is—

$$-\frac{d[M]}{dt} = k_2 \left( \frac{V_{\text{init}}}{k_3} \right)^{\frac{1}{2}} [M] \quad (\text{i})$$

where  $[M]$  is the monomer concentration at any time, and  $V_{\text{init}}$  the velocity of initiation.

This is the usual expression for the disappearance of monomer in a free-radical-initiated polymerisation. As yet nothing can be said regarding any modification of the above equation that might arise owing to the heterogeneous nature of the system. Most probably the reaction rate will be modified significantly by the diffusion of monomer into the nylon and other similar diffusion processes.

From equation (i) it can be deduced that the activation energy of the system is  $E_2 + \frac{1}{2}E_1 - \frac{1}{2}E_3$ . The term  $E_2 - \frac{1}{2}E_3$  is usually small<sup>15</sup> compared with  $\frac{1}{2}E_1$ , so the calculated activation energy of  $13 \pm 1$  kcal./mole is  $\frac{1}{2}E_1$ . A value for the activation energy for decomposition of the "peroxidic" material of 26 kcal./mole is thus calculated, and is of the same order as corresponding values for the decomposition of other organic peroxides (ca. 30 kcal./mole).

In agreement with recent Russian work<sup>14</sup>, the solubility of nylon with a 10% graft of methacrylic acid was greatly decreased, in all the common solvents for nylon, e.g. hot benzyl alcohol or formic acid; in fact, no solvent for the material was found. Irradiation of nylon in air, with radiation doses of the order that was used in the grafting, did not produce any insolubility of the material in these solvents. The electrical surface resistance of the grafted nylon was one-tenth to one-fiftieth that of ungrafted nylon (Table I). Although this is a

marked difference, it is not sufficient to dissipate the large electrical charges which are built up on nylon.

TABLE I  
Resistance Measurements

Nylon Material	Grafted Methacrylic Acid (%)	Surface Resistance of a Square (ohms)
Yarn	0	$1 \times 10^6$
Yarn	24	$1 \times 10^{15}$
Yarn	7	$3 \times 10^{15}$
Fabric	0	$2 \times 10^{12}$
Fabric	9	$4 \times 10^{11}$

\* \* \*

The authors wish to record their thanks to Mr. J. Easy, who helped with the experimental work.

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#### References

- Ballantine, D. S., *et al.*, *J. Polymer Sci.*, **19**, 219 (1956).
- Idem, *ibid.*, **23**, 903 (1957).
- Chapiro, A., *et al.*, *FP* PV690,659 and PV692,736.
- Chapiro, A., *J. Chim. phys.*, **52** (No. 3), 246 (1955).
- Idem, *J. Polymer Sci.*, Discussion (Part 2), 321 (1957).
- Idem, *ibid.*, **34**, 481 (1959).
- Idem, *ibid.*, **34**, 439 (1959).
- Immergut, E., 133rd Meeting of the American Chemical Society, 13th April 1958.
- Ballantine, D. S., *et al.*, *J. Polymer Sci.*, **34**, 419 (1959).
- Cooper, W., and Vaughan, G., *ibid.*, **37**, 241 (1959).
- Burlant, W. J., and Green, D. H., *ibid.*, **28**, 252 (1958).
- Sumitomo, H., *J. Chem. Soc. Japan.*, **62**, 132 (1959).
- Whyte, R. B., and Melville, H. W., *J.S.D.C.*, **65**, 703 (1949).
- Korshak, V., *Doklady Akad. Nauk. S.S.S.R.*, **122**, 122 (1958).

## The English Contribution to the Early History of Indigo Printing

(The late) P. C. FLOUDD

An examination has been made of the early uses of the tepid indigo fermentation vat and its consequent use with resist techniques, culminating in the use of metal blocks for the printing of the wax resist. A description is given of the important English contributions to the early history of indigo printing, firstly by the use of "penciling", and secondly by the "china-blue" technique of direct printing with indigo.

In the first article we examined the evidence concerning the origins of calico printing in England at the end of the seventeenth century, and in the process considered the problem of why the discovery of printing with fast colours, using a mordant technique with madder, was so long delayed in Europe by comparison with India. In this article we shall consider the development of indigo dyeing and printing, which ran parallel with the madder style, and together with it formed the basis of all calico printing up to the end of the eighteenth century.

The questions involving indigo printing are complicated enough in themselves, but have unfortunately been rendered much more so by being misunderstood by some of the leading

writers on calico printing, in particular by R. Forrer, whose two standard and often-quoted works<sup>1</sup> contain the strangest confusions between mordant techniques and indigo-resist techniques. Moreover these problems have hardly been touched on by any English writers, which is the more to be regretted because it was in this special field of indigo printing that the early English printers made their most striking contributions to the whole development of European textile printing. If it has been possible in this article for the first time to set out in English the issues involved—though certainly not to provide all the answers—this is very largely due to the recently published researches of Monsieur P. R. Schwartz, of the Musée de l'Impression sur Étoffes, at



Mulhouse, France, which have clarified many of these questions<sup>2</sup>.

Early calico printing can only be understood if account is taken from the start of the fact that madder and indigo, the two basic vegetable dyestuffs, involve two quite different techniques. As is well known, madder will only "take" on cotton cloth previously prepared with suitable metallic mordants, but has the exceptional property of producing a variety of different colours according to the strength and composition of the mordant. It is, of course, just this special characteristic which suited it so eminently to the production of multi-coloured patterns, and enabled the Indian chintz-painters, and later their European imitators, to base their output on the manipulation of madder, constantly astonishing the layman by their capacity to produce a whole range of blacks, purples, browns, violets, and reds from a single dyeing. The special properties of indigo, by contrast, particularly suited it to piece-dyeing, while making its use for coloured patterns exceptionally difficult.

This difficulty arose from the fact that indigo is insoluble and cannot therefore be used to impregnate cloth by a normal dyeing process<sup>3</sup>. Two separate stages are required: the indigo must be reduced to soluble "indigo white" for the purpose of the impregnation, and then reoxidised to indigo in air to obtain the fast colour. This double process presented no problem for *piece* dyeing, for the total immersion of the cloth in the vat ensured that the impregnation was completed before the subsequent reoxidation began. In "penciling" or block printing, by contrast, the indigo white taken up from the vat on brush or block began immediately to be transformed back into insoluble indigo on its passage through the air, so that by the time it reached the cloth no impregnation was possible and the whole operation was abortive.

So intractable was this problem that the Indians—and equally the Indonesian batik-dyers—never succeeded in solving it, and were therefore never able to produce blue patterns direct on white cloth. They were limited to white patterns on blue, obtained by covering the white areas with a resist paste and then piece-dyeing the whole cloth in the ordinary way. Recent research by John Irwin of the Victoria and Albert Museum<sup>4</sup> has shown for the first time that the traditional Indian chintz-patterns—no doubt because of this difficulty—had dark grounds with the white forming only a small part of the pattern. Only after Indian chintzes had become popular in Europe, and the East India Companies had begun the practice of sending out designs from Europe, was there a switch-over to the white-ground patterns which we normally associate with the word "chintz". For these the Indians had to go through the infinitely laborious procedure of covering perhaps 90% of the whole area with the resist paste as the only means of obtaining the small areas of blue—for flowers and the like—required by the European designs. Such a procedure would have been far too costly if practised in Europe, and the story of the use of indigo in the

early stages of European calico printing therefore resolves itself into a search for a means of printing indigo direct. No fewer than six successive stages in this process can be traced, in most of which the English printers seem to have played a leading rôle.

The first stage involved no more than the introduction into Europe of resist-dyeing methods comparable to those used in India. The mediaeval European blue-dyers had never managed satisfactory resist patterns. This was because they were dependent on the use of woad, which, being a much weaker dye than indigo, had to be used at a temperature (about 170°F.) which was so high that any resist paste containing fat or wax melted in the vat. As soon as indigo began to be imported in large quantities in the seventeenth century, it became possible, either by mixing indigo with the woad, or better still by using the indigo alone, to reduce the necessary temperature to no more than 115°F. and thus, for the first time, to copy the traditional Indian resist-paste techniques<sup>5</sup>. There is no conclusive evidence to show when or where this Indian tepid indigo fermentation-vat was first introduced into Europe, though it seems probable that it was already known by the last quarter of the seventeenth century.

A second step forward, and in this case one going beyond the Indian technique, was the replacement of this tepid vat by a really cold vat based on the reduction and dissolution of the indigo by means of copperas (ferrous sulphate), lime, and potash. (The lime combines with the ferrous sulphate to form calcium sulphate, and ferrous hydroxide which reduces the insoluble indigo to the soluble indigo white.) Here again there is no positive evidence concerning the exact time and place of this advance, but Monsieur Schwartz has drawn my attention to the significance of a footnote in the 2nd edition of Edward Bancroft's classic *Experimental Researches concerning the Philosophy of Permanent Colours*<sup>6</sup>, in which he states that some earlier papers which he had studied showed that the use of this ferrous sulphate vat, at least for linen printing, was already known, though perhaps not properly understood, in England in 1734. As far as I am aware, this is the earliest known reference to the ferrous sulphate vat.

Parallel with this development in the chemistry of indigo dyeing went various mechanical innovations which enabled the European printers to print wax as a resist by means of blocks rather than laboriously to paint it on by hand as in India. Wood blocks, of the sort used for the printing of the madder mordants as described in the first article, were obviously unsuitable for hot wax, and had to be replaced by metal blocks made from a mixture of tin, lead, and pewter. Their use, in conjunction with a printing table strewn with sand in order to absorb the molten wax and to prevent it spreading, is clearly described in the earliest known book on European calico printing, published in Paris in 1760<sup>7</sup>, and a recent French writer has categorically stated that the procedure was first introduced by printers at Rouen in 1709<sup>8</sup>. This cannot, however, be accepted, for a German

book published as early as 1686 actually includes a section with the specific title "How to make lead blocks for printing cotton"<sup>9</sup>. An obscure Continental reference to the printing of wax resist with metal blocks in England even appears to carry the practice back to the early seventeenth century, though this probably originally referred to the rather different procedure for the printing of wax resist on silk<sup>10</sup>.

In any case the tangible evidence of many surviving textiles shows that by the mid-eighteenth century at the latest the block printing of wax-resist designs on cotton (or more frequently on linen), followed by a cold indigo dyeing, was a standard practice for the production of rather crude white-on-blue designs of a semi-peasant sort all over Europe. A well-known German group with religious designs and inscriptions is represented by examples in many collections<sup>11</sup>, and the type seems to have subsisted in Central Europe until well into the nineteenth century.

Mention should also be made of a quite different and most puzzling group of blue-and-white prints which have been the subject of much discussion—but so far entirely inconclusive. Their most peculiar characteristic, which differentiates them from all the normal Central European indigo-resist prints, is that although they equally are resist-dyed, with the white areas resist-printed and the blue areas piece-dyed, it is nevertheless the blue which forms the design and the white the background. Almost all the surviving examples have been found in the area round the Hudson valley, which has convinced several American authorities that they must have been produced there. However, this seems quite incompatible with what one knows of American dyeing resources in the early eighteenth century—the period from which these textiles are believed to date. Moreover, one typical example bears an unmistakable English excise stamp for 1766 (see Fig. 1), which can be taken as positive proof that this piece at least must have been printed in England<sup>12</sup>. It would be satisfactory to think that the whole group were English, but in that case it seems extraordinary that they never turn up in England—or indeed in Europe generally. Until some further positive evidence is assembled, they will remain a mystery.

Whatever the final attribution of these American "blue resist" prints, there seems little doubt that, whereas the wax-resist technique continued to flourish in France, Germany, and Switzerland up to and beyond the end of the eighteenth century, and in Poland and Slovakia even later<sup>13</sup>, it was already obsolescent in England much earlier in the century. This is clearly shown by a curious passage in Samuel Parkes's *Chemical Essays* (1815)<sup>14</sup>, in which he describes how three or four years earlier a huge dump of mixed flour and wax and gum was found outside Stockport. At first it caused much speculation and was thought to be some strange natural phenomenon, until it was remembered that seventy or eighty years earlier the wax-resist technique had been used by local calico printers, whose debris this was.

The main reason for the early disappearance of wax-resist printing in England was the fact that the English printers were undoubtedly the first to discover satisfactory methods for printing indigo direct, and thus dispensing with resists—whether painted or printed. This was perhaps the most decisive advance in the early history of European textile printing. As usual the evidence for the primacy of the English printers comes almost entirely from non-English sources, and rests perhaps most definitely on the fact that two totally different methods for printing indigo were both called on the continent "bleu d'Angleterre" or "Englischblau". It is only thanks to Monsieur Schwartz's analysis of all the original sources that it is now possible to disentangle the two methods and their parallel development.

The first printable indigo—called in England "pencil blue"—was achieved by adding orpiment (arsenic trisulphide) to the ferrous sulphate vat (together with gum Senegal as a suitable thickener). It was found that this addition delayed the reoxidation of the indigo during its passage from vat to cloth just long enough to allow it to be effectively painted on with a brush. It seems that this innovation must have been introduced almost simultaneously with the ferrous sulphate vat itself, that is in the 1730's. Persoz had a fabric which he claimed to have been printed in "pencil blue" in Switzerland in about 1730<sup>15</sup>, and Jean Ryhiner, the Basle printer, in his *Journal*, gives full details of how a firm of colourmakers in Bremen offered his father's firm a routine receipt for "Englischblau" incorporating the use of orpiment in 1745<sup>16</sup>.

It seems that this "pencil blue" was never entirely satisfactory. In the first place the use of the arsenical compound presented many dangers both to the men working at the indigo vats and to the women and children who were employed as "pencillers" to paint it on. In the second place it could only be painted on stroke by stroke, so that large areas always looked messy and uneven, as with a fast-drying water-colour. Thirdly it could not be easily used for block printing, for the effect of the orpiment was not sufficiently strong to delay the reoxidation of the indigo long enough to allow it to be spread on the surface of the tub ready for the block.

This third difficulty was partly circumvented by the two mechanical contrivances known as the "spring-sieve" and the "closed tub". The standard method for printing madder mordants by wood block involved the use of a "tub" and a "sieve", the purpose of which was to provide some elasticity in the surface against which the block was pressed down in order to take up the mordant before each printing. The "tub" consisted in England of a sawn-off barrel, although on the Continent a specially constructed square "tub" was more normal. This was filled with a viscous paste made from discarded colour and gum, known in the trade as the "swimmings". On this elastic cushion rested the "sieve"—a wooden drum just a fraction smaller than the "tub", the bottom surface of which was a sheepskin, and the top surface a



FIG. 1.—A typical example of a puzzling group of "blue resist" textiles found in many American collections but of disputed origin. This piece, in the collection of the Albany Institute of History and Art, is unique in bearing an English excise stamp for 1766, and must therefore have been printed in England.

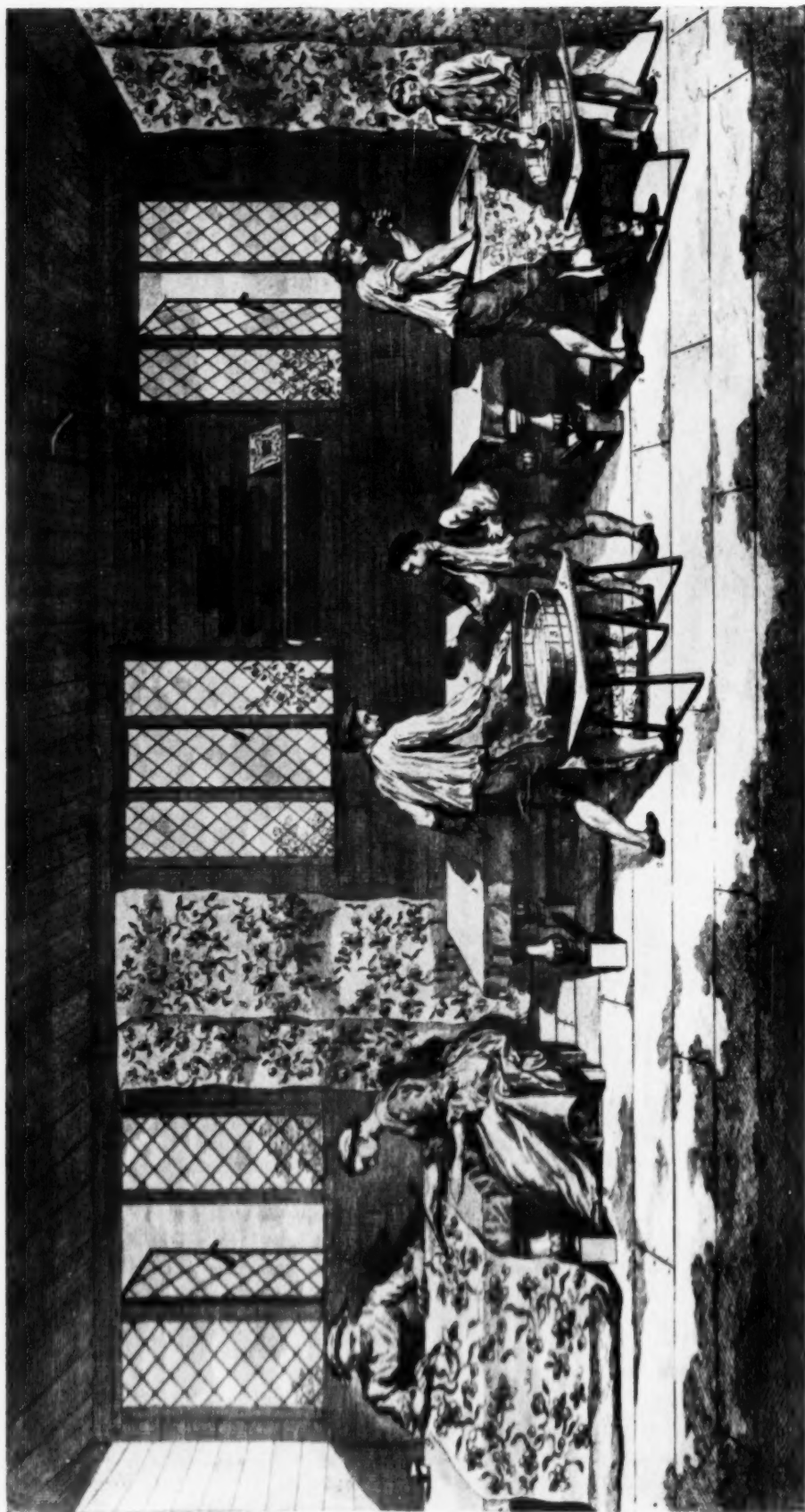


FIG. 2.—An eighteenth century English printworks, showing two wood-block printers with their boy "carriers", and two women "pencillers" painting in additional colours.  
From the Supplement to John Barrow's *New and Universal Dictionary of Arts and Sciences* (London 1754)





FIG. 4





FIG. 5.—An early example of English "china-blue" printing from engraved copper plates. The textile, in the Victoria and Albert Museum, can be identified as the work of the Bromley Hall printworks from its correspondence with a paper impression, also in the Museum, marked "Country Village 10d. per yard. Talwin & Foster" (the proprietors of the Bromley Hall works). The border, which is an example of "china-blue" wood-block printing, is identical with a fragment attached to a business letter dated 1749 in the Library of the New York Historical Society.

tightly stretched finely-woven woollen cloth. A boy "tearer" (from the French *tireur*) kept the top surface of the sieve constantly and evenly supplied with the thickened mordant which he spread on with a large brush. When the printer pressed his block down in this, the "swimmings" provided just enough "give" to ensure the satisfactory colouring-up of the block. (The whole arrangement is clearly shown in a beautifully engraved Plate (see Fig. 2) issued with the Supplement to John Barrow's *New and Universal Dictionary of Arts and Sciences* (1754).)

The indigo "spring-sieve" involved a basic simplification of this standard equipment, with the aim of keeping the indigo from contact with, and therefore from reoxidation by, the air. The "tub" remained unchanged, but the "swimmings" were replaced by the thickened indigo itself. The "sieve" was no longer a drum with stretched surfaces at top and bottom, but merely a single stretched surface floating directly on the indigo and protecting it from contact with the air. The task of the "tearer" in spreading the colour on the surface was now superfluous, for when the printer pressed down his block the thickened indigo seeped up through the cloth and coloured the block directly. After the removal of the block the "tearer" merely had to scrape any remaining reoxidised indigo off the surface. The necessary corollary to the "spring-sieve" was the "closed tub", which was a simple device for keeping the level of the indigo in the tub more or less constant by means of a tap and a gravity feed from an air-tight reservoir.

It is impossible to give a precise date or place for the introduction of these innovations. On the one hand Monsieur Schwartz has traced a reference to the orpiment vat being used for block printing as early as 1764<sup>17</sup>, which would lead one to suppose that some such device as the spring-sieve was already in use by then. On the other hand there is clear evidence from both France and England that the block printing of "pencil blue" was still being regarded as an unsolved problem even after 1800. In France, for example, the Société d'Encouragement pour l'Industrie Nationale announced in 1806 that Oberkampf, the famous Jouy printer, had offered a prize of 1,200 fr. for the development of an indigo which could be satisfactorily block-printed<sup>18</sup>. In England the evidence is rather more confused. O'Brien, whose book<sup>19</sup>, being mainly concerned with routine details of workshop practice, would be expected to say something on the subject, has nothing except a passing reference to the use of "wired sieves and agitators" in indigo block-printing, which sounds like some even more primitive device than the spring-sieve. Parkes, on the other hand, as late as 1815<sup>20</sup>, illustrates a straightforward spring-sieve and closed tub (see Fig. 3), but speaks of them as having been only recently perfected, and his claim that a personal friend had recently been the first to invent a method of ensuring "that the canvas should follow the colour as it wasted", implies that the details of the device were still being worked out. It seems fairly clear therefore that the very

real problems involved in block-printing "pencil blue" were still not solved at that date, either in France or England.

Fortunately for the eighteenth century printers, an entirely different method of printing indigo had been developed in the meantime. This, though indiscriminately called "bleu d'Angleterre" on the

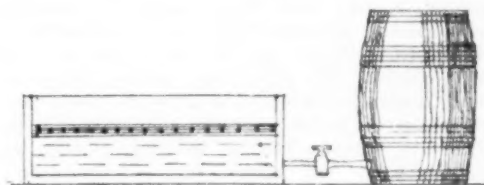


FIG. 3

Continent, was differentiated in England as "china-blue". By contrast with the various developments which we have so far discussed, each of which could have been arrived at in the normal course of workshop trial-and-error, "china-blue" printing involved a noteworthy and different chemical technique. It is therefore particularly satisfactory that in this case at least we can provide some independent and tangible evidence to support the traditional Continental assumption that it was first discovered in England.

Whereas the "pencil blue" process depended on trying to retain the indigo in a state of solution during its passage from the vat to the cloth, "china-blue" was based on the radically different principle of printing the indigo in an undissolved state, and then arranging its simultaneous reduction and solution on the cloth *after* printing. In practice this meant printing the indigo, mixed with ferrous sulphate and thickened, as a finely-ground paste, and then alternately immersing the printed cloth in a bath of lime (to dissolve the indigo) and a bath of ferrous sulphate (to reduce it) as many times as necessary to achieve the desired strength of blue. Although this process was complicated in its chemistry, it was physically simple. The printing of the ground indigo, either by wood block or by copper plate (as will be described in the next article) involved no special devices as with "pencil blue", and the subsequent operations required nothing more difficult than a series of racks for holding the cloth in folds so as to facilitate the alternate immersions. Strangely enough I have only been able to trace a single illustration of "china-blue" printing, and that in an English publication as late as the 1870's<sup>21</sup> (see Fig. 4). This shows three baths (the standard lime and ferrous sulphate baths and a third caustic soda bath to remove excess ferric hydroxide precipitated by the second bath) in the form of stone cisterns sunk into the floor, with the cloth being shifted from one to another on a special frame. Some similar labour-saving arrangements must have been worked out when the process was first developed well over a century earlier.

The "china-blue" technique involved disadvantages as well as advantages by comparison with "pencil blue", and did not therefore supersede

the earlier method. Both processes remained in simultaneous use, for different purposes. The great advantage of "china-blue" was that it could be evenly printed with a high degree of definition, by contrast with the smudgy unevenness which was hardly avoidable with "pencil blue". The main disadvantage was that the successive immersions after printing damaged madder colours and thus made it virtually impossible to combine them with "china-blue". Inevitably, therefore, "pencil blue" continued to be used well into the nineteenth century wherever small touches of blue (and of green, by the superimposition of yellow over the blue) were to be added to already-printed madder colours to produce what was known as a "full chintz", whereas "china-blue" was developed for blue monochrome designs.

It is this application of "china-blue" to monochrome blue designs which lends special significance to two groups of textiles which first came to light during the author's visit to the United States in 1957. The first group consists of some tiny fragments attached to a letter dated 1749<sup>22</sup> in the Alexander correspondence in the Library of the New York Historical Society. Reference was made in the first article to a similar group of fragments attached to a letter dated 1726, which, however, include no examples of blue printing. The 1749 fragments by contrast include several delicate little linear designs very neatly printed in an even blue which must certainly be examples of "china-blue"<sup>23</sup>. Their special interest lies in the fact that their discovery enables us to establish the existence of the style at least fifteen years before the earliest known description of it, for Monsieur Schwartz has so far found no reference earlier than 1764<sup>24</sup>.

While these little New York fragments thus throw some welcome light on the question of the date when "china-blue" could first have been introduced, the other group of textiles found in the United States provided unexpectedly copious support for the theory that the place of its introduction must have been England. This latter group consisted of no less than forty-five "china-blue" textiles printed from copper plates by English printworks between 1760 and 1790, which were found during examination of the large collections of printed textiles in museums in Winterthur (Delaware), New York, Boston, and Philadelphia<sup>25</sup>, and among the collections at Colonial Williamsburg and elsewhere (see Fig. 5). The significance of this group can best be judged by comparing it with the sum total of ten designs printed in blue which is all that I have succeeded in tracing among the Continental (and principally French) output of copper-plate prints over the same period. No doubt others exist, but monochrome blue copper-plate designs were certainly regarded as quite exceptional. Oberkampf at his celebrated Jouy factory seems to have produced no more than three or four, and the firm of Favre Petitpierre of Nantes, who apparently issued more copper-plate designs than any other printworks in France, never printed any in blue<sup>26</sup>.

It may be wondered why all these early English "china-blue" textiles, found in the United States, were printed from copper plates rather than from wood blocks. The reason cannot be that the "china-blue" technique was unsuited for use with wood blocks, for we have the tangible evidence of the 1749 fragments, which are certainly block-printed. The real explanation must be sought in the joint operation of two factors. On the one hand, the disadvantage that "china-blue" could not be combined with madder colours, though a serious limitation for the wood-block printers, was no handicap at all to the copper-plate printers, who, for technical reasons to be discussed in the next article, were in any case limited to monochrome designs. On the other hand, that sharp definition which was the special advantage of "china-blue" over the smudgy unevenness of "pencil blue", could be far more effectively exploited in copper-plate printing with its finely engraved lines and crisp drawing than in the bold but relatively coarse technique of the wood block<sup>27</sup>. As a result of these two considerations it became the practice of the eighteenth century English printers to use "china-blue" almost exclusively for monochrome copper-plate designs, while relying on "pencil blue" for polychrome prints.

We can best conclude by summarising our findings about the six successive stages which we have traced in the complicated development of early European indigo-printing. First came the supersession during the seventeenth century of the traditional European wool-dyers' hot woad fermentation-vat by the traditional Indian cotton-dyers' tepid indigo fermentation-vat, and its consequent use with resist techniques. Second came its replacement in turn by the really cold ferrous sulphate vat—perhaps first developed in the 1730's. Third was the use of metal blocks for printing the wax resist—which cannot be dated at all precisely but was certainly known by the middle of the eighteenth century. Fourth was the discovery of "pencil blue" by the addition of orpiment to the ferrous sulphate vat—also probably in the 1730's. Fifth came the invention of the spring-sieve and the closed tub—innovations which it has so far proved impossible to pin down exactly in either time or place. Sixth and finally, the discovery of "china-blue"—the culmination to this whole sequence, and the advance which does most credit to those English chemists and printers who were almost certainly the first to develop it in the 1740's.

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(Received 28th July 1959)

#### Notes

<sup>1</sup> Robert Forrer, *Die Zeugdrucke der byzantinischen, romanischen, gotischen und späteren Kunstepochen* (Strassburg 1894), and *Die Kunst des Zeugdrucks vom Mittelalter bis zur Empirerzeit* (Strassburg 1898).

<sup>2</sup> "Contribution à l'Histoire de l'Application du Bleu d'Indigo (Bleu Anglais) dans l'Indiennage Européen", *Bull. Soc. industr. Mulhouse*, 63-79 (Nov. 1953).

- <sup>3</sup> The clearest general statement of the problems of indigo printing and dyeing are to be found in J. Persoz, *Traité théorique et pratique de l'impression des Tissus* (Paris 1846), Vol. III, pp. 14-87.
- <sup>4</sup> *Journal of Indian Textile History* (Ahmedabad), (1), 14 (1955).
- <sup>5</sup> See Adolf Jenny-Truempy, "Handel und Industrie des Kantons Glarus" in *Jahrbuch des Historischen Vereins des Kantons Glarus*, 34, 53 (1902).
- <sup>6</sup> 2nd edition, 1813, Vol. I, p. 211.
- <sup>7</sup> *Traité sur les Toiles Peintes par M.Q\*\*\** (Amsterdam and Paris 1760), p. 108. This work, which was written by the Chevalier de Querelles, was issued in a facsimile reprint by the Badische Anilin- und Soda-fabrik (Ludwigshafen am Rhein 1925).
- <sup>8</sup> Pierre Dardel, *Les Manufactures de Toiles Peintes et de Serges Imprimées à Rouen et à Bolbec aux XVIIe et XVIIIe siècles* (Rouen 1940), p. 14.
- <sup>9</sup> Gottfried Schultze, *Schatzkammer rarer und neuer Curiositäten* . . . (Hamburg 1686), p. 312. I have been unable to trace a copy of this work in England, but quote from Karl Reinking and Louis Driessen, "Die ältesten Bücher über den Zeugdruck", Part III, in *Melliand Textilber.*, 10, 959 (Dec. 1929). It is true that Schultze's sectional title does not actually state that the lead blocks were used for the printing of a hot wax resist. It is, however, difficult to conceive for what other purpose they would have been devised.
- <sup>10</sup> C. F. Kreisig, *Die Zeugdruck und die damit verbundene Bleicherei und Färberei* (Berlin 1834-7), Vol. III, p. 462, quotes "McKernan" as describing wax-resist printing on silk and linen with metal blocks in England "two hundred years earlier". I have, however, been unable to trace any such statement in H. Mackernan, *Treatise on Printing and Dyeing Silk* (London 1829), to which Kreisig was presumably referring.
- <sup>11</sup> For illustrations see Erich Meyer-Heisig, *Weber, Nadelwerk, Zeugdruck* (Munich 1956).
- <sup>12</sup> In the collection of the Albany Institute of History and Art. Another piece from the same design, but without the excise stamp, is in the collections at Colonial Williamsburg. The date of 1766 is given by the code-number "54" in the stamp, which indicates the fifty-fourth year after the original imposition of the excise on printed goods in 1712.
- <sup>13</sup> For Poland see Roman Reinfuss, *Polskie druki ludowe na plotnie* (Warsaw 1953). For Slovakia see Josef Vydra, *Indigo Blue Print in Slovak Folk Art* (Prague 1954).
- <sup>14</sup> Vol. II, p. 149.
- <sup>15</sup> *Op. cit.*, Vol. III, p. 55. Persoz gives the printer's name as "Labrane", although it appears to have been actually Jean Labran (see Alice Dreyer, *Les Toiles Peintes en Pays Neuchâtelois* (Neuchâtel 1923), p. 26).
- <sup>16</sup> Although long extracts from Ryhiner's Journal were published by Dollfus-Ausset in his *Matériaux pour la Coloration des Étoffes* (Paris 1865), these particular details remained unpublished until the appearance of Monsieur Schwartz's 1953 article.
- <sup>17</sup> *Op. cit.*, p. 69.
- <sup>18</sup> *Bulletin de la Société d'Encouragement pour l'Industrie Nationale*, 5, 237 (1806). The offer was repeated in 1809 and finally withdrawn in 1810. Two candidates for the prize came forward, but neither satisfied the qualifications for an award (*ibid.*, 8, 273).
- <sup>19</sup> Charles O'Brien, *The British Manufacturers Companion and Calico Printers Assistant* (1792).
- <sup>20</sup> *Chemical Essays* (London), Vol. II, p. 153 and Plate VIII.
- <sup>21</sup> G. W. Yapp, *Art Industry: Furniture, Upholstery and House Decoration* (London n.d.), p. 73 and Fig. 9.
- <sup>22</sup> Letter dated 2nd October 1749 from New York to David Barclay & Son, one of the largest London export agents. The fragments accompany repeat orders for printed textiles.
- <sup>23</sup> Among these fragments are two tapes, printed in blue from wood blocks, with designs identical to those found on many copper-plate printed curtains and hangings in American collections, and known to have been printed by leading London printworks such as Francis Nixon, or the famous Bromley Hall works. An example is illustrated in Fig. 5.
- <sup>24</sup> The reference occurs in Vol. II of a *Dictionnaire portatif des Arts et Métiers* published in Paris in 1766, but already approved for publication two years earlier. The reference was discovered after the appearance of the 1953 article, and is not, therefore, mentioned in it.
- <sup>25</sup> The Henry Francis du Pont Winterthur Museum, the Metropolitan Museum, and the Cooper Union Museum in New York, the Museum of Fine Arts in Boston, and the Museum of Art in Philadelphia.
- <sup>26</sup> Henri Clouzot, "Les Toiles Imprimées de Nantes—Rivales des Toiles de Jouy", in *La Renaissance de l'Art Français* (1924), Vol. VII, pp. 605-616.
- <sup>27</sup> For reasons which are not entirely clear it seems also that "china-blue" did not work well where large areas of blue were required, so that in practice it was limited either to copper-plate prints or to wood-block prints with similar linear designs.

## EXTERNAL ADDRESS

### A New One-bath Method for Continuous or Pad-Roll Vat Dyeing\*

F. L. J. VAN LAMOEN and H. BORSTEN

A description is given of a new one-bath method for continuous vat dyeing, which can be used in both pad-steam installations and Pad-Roll machines. Although at present the full details concerning the best procedure are not available, it is expected that the method developed for the continuous vat dyeing of relatively short lengths of cloth will prove most suitable for Pad-Roll machines.

#### Introduction

From an economic point of view the use of the majority of the well-known continuous vat-dyeing processes is justified only in dyehouses having a very large production of vat-dyed goods with a limited number of colours<sup>1</sup>. In principle it is only with the Standfast molten-metal process that it is possible to dye shorter lengths economically, especially in the case of light-weight cloth. This method, however, has certain disadvantages. Further investigation was therefore made, in order to arrive at a new method of dyeing economically

shorter lengths of cloth (5000 metres) with vat dyes, continuously or semi-continuously. We started with the following considerations in mind.

(a) One of the difficulties encountered in the various continuous vat dyeing methods is the fact that, in general, leuco vat dyes have high affinity for cellulosic material, and the affinity differs from dye to dye. Consequently it is necessary to apply the vat dye to the cloth in an unreduced form.

(b) A second difficulty inherent in the chemical pad—used in pad-steam processes and in certain cases during the molten-metal process—is the

\* Paper presented at the I.F.A.T.C.C. Congress held at Church House, Westminster, 16-18th September 1959.



reduction and bleeding of part of the dye from the pigmented fabric. Consequently it is advisable for the vat dye to be padded on to the cloth in an unreduced form, together with the chemicals required for reduction of the dye<sup>1</sup>. If this could be achieved, the following advantages associated with pigment padding of the dye would be retained—

- (i) No substantivity of the vat dye
- (ii) Better uniformity of the dyeings
- (iii) Better penetration
- (iv) Possibility of deep colours.

Moreover, in the normal pad-steam process, the use of a bath of the above composition has the advantage that the drying procedure which is often included can be omitted.

(c) During every continuous vat dyeing, it is necessary to reduce and/or fix the vat dyes with the reducing agents present by applying a heat-treatment with the exclusion of air. Consequently, if a fabric, padded with a solution as indicated under (b), is steamed in a normal steamer within a reasonable time, reduction and fixation of the vat dye must take place. Thus the reducing chemicals must have no action on the vat dye at room temperature, but preferably rapid reduction must occur when the temperature is raised. As the new method was intended for the dyeing of relatively short lengths, the steaming time could be somewhat longer than is the case in the normal pad-steam process.

(d) The reducing medium must not be so stable that oxidation of the dyeing takes much longer or requires a greater quantity of oxidising chemicals than is the case in normal continuous dyeing processes.

(e) Finally, the dyeings must be finished in the normal way.

In connection with the development of the new method, it was found that, if an attempt was made to use the plant available in the larger dyehouses, certain items of machinery would have to be altered to meet the specific requirements of the process. Therefore it is not surprising that, although it was intended to develop the new method on a fully continuous scale, during more recent experiments greater attention has been paid to a practical development using a Pad-Roll machine<sup>2-4</sup>. This does not imply, however, that a fully continuous process is impossible. Some large-scale experiments have shown that a pad-steam installation can give satisfactory results.

### Principle of the Dyeing Method Developed

#### INTRODUCTION

As starting point we chose the well known potassium carbonate-sulphoxylate formaldehyde vat printing method. In these experiments we were able to use the knowledge gained in our previous investigations on redox potential measurements during vat dyeing<sup>5</sup>.

During vat printing a thickening containing potassium carbonate and the reducing agent is applied to the fabric. It may be assumed that in many cases the vat dye in the print paste remains unreduced or is only partly reduced at room

temperature. However, if the temperature rises, the reduction potential will reach such a negative value that complete reduction, as well as fixation, will occur.

From experiments carried out by Marshall and Peters<sup>6</sup>, it is evident that the reduction potential of print pastes depends on the alkalinity, as well as on the nature and concentration of the reducing agents and on the temperature.

The use of the leuco potentials of vat dyes, as introduced by these authors<sup>7</sup>, proved to be of great importance during our investigations. From the information in these papers<sup>6,7</sup>, the requirements to be met by a reducing bath as given under (c) are as follows: the potential of a bath containing both unreduced vat dye and reducing chemicals must be less negative than the leuco potential of the vat dye at the concentration used during padding. On raising the temperature the reduction potential of the bath should fall well below the leuco potential of the vat dye at the concentration used. It is evident that, during the heat-treatment, air must be excluded, as in steaming.

With an ideal leuco potential curve the reduction of vat dyes at room temperature is impossible, as is illustrated in Fig. 1. With a non-ideal curve (Fig. 2), as occurs with a large number of vat dyes<sup>6</sup>, theoretically the potential value *A* at room temperature is to be preferred to value *C*. However, it is clear that, when a reducing bath having a potential *A* is used, a certain amount of reduction of the vat dye will be unavoidable, and the objective, viz. no reduction of the vat dye in the cold, will not be attained.

It should be noted that not only the bath potential, but also the leuco potential, depends on the temperature, and the leuco potential depends also on the concentration of vat dye in the bath.

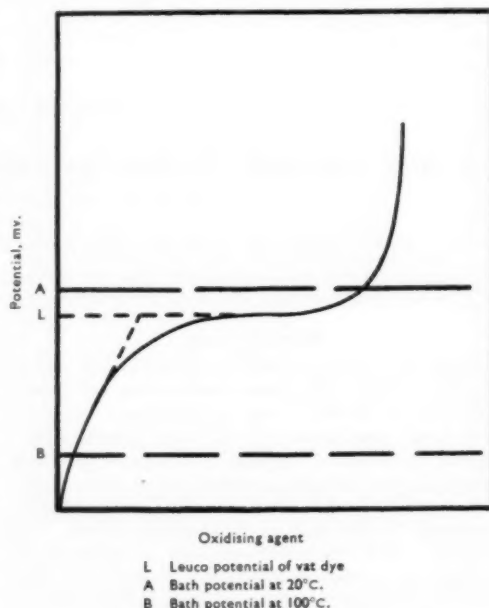


FIG. 1—Ideal Leuco Potential Curve



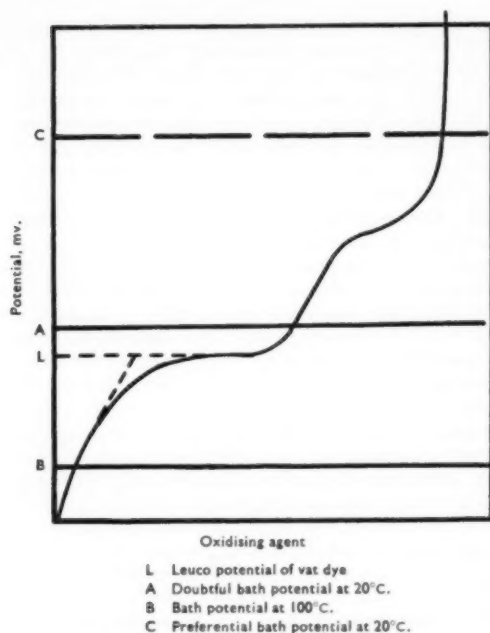


FIG. 2—Non-ideal Leuco Potential Curve

This can be deduced theoretically as well as from the literature<sup>9</sup>. A higher temperature or a higher concentration of dye will give a more negative leuco potential. It follows, therefore, that the bath potential at a given temperature has to be chosen in relation to the leuco potential of the given concentration of vat dye at the same temperature. Reduction will take place only if at the higher temperature the bath potential reaches a more negative value than the leuco potential of the vat dye.

No account is taken of the rates of reduction of the vat dyes, although this factor may be important during the technical application of a reducing medium meeting the requirements outlined.

#### PROCEDURE

##### The Reducing Bath

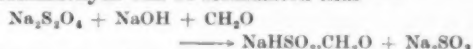
Increase in alkalinity usually lowers the reduction potential of reducing baths based on hydrosulphites. Since a reducing agent was required which would not have a lower reduction potential at the low temperatures and high alkali concentrations used in continuous vat dyeing processes, sodium hydrosulphite could not be used. Special attention was therefore directed to the use of sodium sulphonylate formaldehyde. Although this compound is a much weaker reducing agent than are hydrosulphites, it was found that, in the presence of high alkali concentrations (4–8% NaOH), the reduction-potential values were so low that many of the usual vat dyes would be reduced at room temperature.

It was therefore necessary to find a reducing agent whose reduction potential at the necessarily high alkalinities of the reduction baths would be less negative than that of sodium sulphonylate

formaldehyde at room temperature. At higher temperatures, however, the reduction potential had to fall to nearly the same value as that reached with the latter reducing agent, otherwise reduction of the vat dye would be incomplete.

It has been found that, if to a bath containing sodium hydrosulphite and sodium hydroxide more formaldehyde is added than is necessary for the formation of sodium sulphonylate, a less negative bath potential can be obtained at room temperature than by using sodium sulphonylate formaldehyde only\*.

The preparation of sodium sulphonylate formaldehyde can be formulated thus<sup>10</sup>—



Hence the reduction bath is a solution containing sodium hydroxide, sodium sulphonylate, and an excess of formaldehyde. This was confirmed by adding a calculated quantity of formaldehyde to a reduction bath containing only sodium hydroxide and sodium sulphonylate formaldehyde. Reduction potentials were obtained which were identical with those of solutions containing sodium hydroxide, sodium hydrosulphite, and formaldehyde based on the formulation given above.

Other alkalis and aldehydes in combination with hydrosulphites gave similar results for the reduction potential of the solutions. For theoretical and economic reasons, however, the combination based on sodium hydroxide, sodium hydrosulphite, and formaldehyde is to be preferred.

The phenomena described above do not depend on the occurrence of a Cannizzaro reaction between the formaldehyde and the alkali, for the addition of methanol or formic acid does not produce changes in potential of a similar character. On the

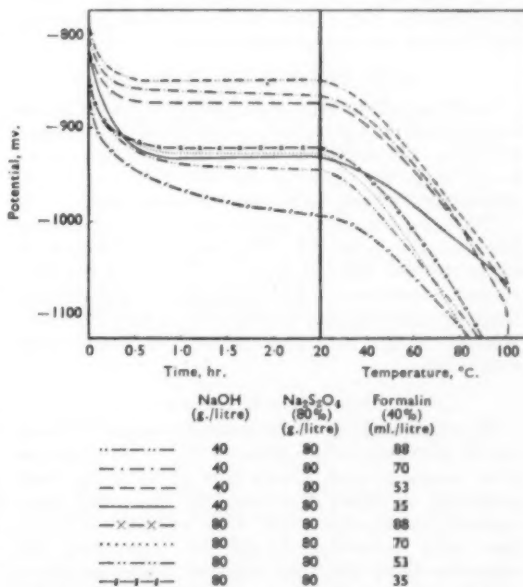


FIG. 3—Reduction Potential of Reducing Baths of Differing Composition as a Function of Time and Temperature

\* Patents applied for.

contrary, a Cannizzaro reaction must be avoided during the preparation of the solutions, as it could lead to consumption of formaldehyde, together with some neutralisation of alkali. Consequently the addition of the different reagents has to be executed in a strict order, viz. sodium hydroxide, sodium hydrosulphite, formalin.

During the preparation of the solution some heat is evolved, so the solutions must be cooled, if necessary, to about 25°C. before use.

The behaviour of solutions of this type of varying composition is illustrated in Fig. 3, from which it is clear that the reduction potentials of different solutions depend on the alkali concentration as well as on the excess of formaldehyde. Most of the commonly used vat dyes can be applied with a reducing solution, the composition of which can be chosen to meet the requirements given previously. The effect of rise in temperature on the reduction potential is also shown in Fig. 3.

The effect of excess formaldehyde on the reduction potential of a dyebath can be explained in terms of change in the equilibrium of the reaction, but as further examination of this reaction was of purely theoretical interest, no attempt was made to check this assumption.

#### DYEING EXPERIMENTS\*

##### General

A large number of dyeings were carried out with a reduction bath of the type described. The dyeing apparatus consisted of a normal horizontal two-roll laboratory pad and a laboratory steam ager, enabling us to dye continuously large yardages of fabrics having a width of about 10 cm.

In addition, some experiments were made on mill-scale continuous-dyeing installations and on a Pad-Roll machine. The results of these experiments, which are of the utmost practical importance, are summarised below.

##### Leuco Potential Measurements

It appears from our experiments to be sufficient to estimate only the leuco potential of a 0.5% dye solution. The values obtained can always be used as a basis for making up the reducing bath, irrespective of the actual dye concentration.

The leuco potentials can be estimated by plotting the change in potential with time while a stream of air is bubbled through a 0.5% solution of the dye, vatted according to the dyemakers' instructions. Only dyes having leuco potentials of 800–1000 mv. relative to the saturated calomel electrode were examined.

##### Preparation of Dyebaths

The composition of the reducing baths is based on the potential values given in Fig. 3. In principle it is chosen in such a way that at 20°C. the bath potential is rather less negative than the leuco potential of the dye used. With mixtures of dyes, the bath potential should be somewhat less negative than the least negative leuco potential of the component dyes. Although this cannot always be achieved, it is advisable in mixtures to

choose vat dyes having approximately the same leuco potentials.

The dyebaths can be prepared as follows—

(a) Half the total volume of water, necessary for dyeing a certain quantity of fabric, is used to disperse the dye. A finely dispersed vat dye powder is to be preferred. If appropriate, certain textile auxiliaries can be added to this dispersion.

(b) The reduction solution contains the total quantity of caustic soda, hydrosulphite, and formalin. The concentrations of these ingredients (added, in the order given, to a volume of water such that the total volume is the same as the volume of the dye dispersion) are thus double the concentrations in the reduction bath chosen. The reducing solution obtained in this way is, if necessary, cooled to about 25°C.

Before starting the dyeing, the two solutions are mixed in a tank, from which the pad is fed. In this tank a stirring device is required to prevent the dye particles from settling out.

The keeping qualities of the solutions are quite satisfactory. Unless the temperature rises above about 30°C., the same bath can be used for 6–8 hr.

The potential of the dyebaths can be measured with a platinum-calomel electrode combination. It has been found in practice that the potential of a dyebath containing the reducing reagents is 35–100 mv. less negative than the potential of the corresponding reducing baths. Although we cannot explain this, it is probably connected with the addition of the more or less ideally reversible vat-dye redox system. In any case, this effect is valuable with dyes having a non-ideal leuco potential curve (Fig. 2). Furthermore, the rise in potential enables us to use dyes having leuco potentials of about 800 mv. with the reducing solution having the most positive reduction potential of about 850 mv. (Fig. 3). This effect is useful also with mixtures of vat dyes having very different leuco potentials.

##### Use of Auxiliaries

The application of textile auxiliaries as wetting and dispersing agents has been investigated in order to ascertain how far certain agents might be of use in large-scale experiments. Only the most popular agents were examined. It was concluded that Setamol WS (BASF) or an identical product may be used as a dispersing agent, whilst a product of the Erkantol BX (FBy) type is suitable as a wetting agent.

The suitability of products such as dextrans, which have some reducing capacity in strongly alkaline media, depends on the leuco potentials of the dyes used.

##### Dyeing Apparatus

**Padding Requirements**—In the laboratory experiments a two-roll horizontal pad was used; in the mill experiments two-roll horizontal and vertical pads were available. In general, all the padding mangles which can be used for the continuous dyeing of direct dyes are suitable for the dyeing process described. During fully continuous dyeing, where a pick-up of 90–100% is required to

\* Use of a product does not imply recommendation of the product to the exclusion of others which may also be suitable.

obtain the best results, some difficulties are encountered with mercerised cloths.

During Pad-Roll dyeing a somewhat lower pick-up is permissible. Padding mangles which give unsatisfactory results during continuous direct dyeing may cause fewer difficulties during the vat dyeing process described, as the dye is in the oxidised form and has no affinity for cellulosic material. However, preferential sorption of either the dye or the vehicle—which may take place in padding and cause tailing—must be avoided, although during the shorter runs for which the process has been developed tailing effects may be of minor importance.

**Reduction of the Dyes**—The reduction of the dyes has been carried out in a laboratory continuous steamer, in a normal pad-steam steamer, and in Pad-Roll steaming chambers. The conditions during steaming in a continuous process must be identical with those during normal pad-steam vat dyeing processes. To obtain the best results from the point of view of colour yield and levelness, however, the steaming time must be longer than during normal continuous pad-steam vat dyeing processes, e.g. 0.5–1.0 min.

During steaming in a Pad-Roll chamber, completely saturated, air-free steam at 100–101°C. is required, otherwise oxidation or other dyeing faults will result. It has been found possible to exclude air completely by altering the position, and increasing the number, of the steam valves, thus increasing the amount of steam injected to drive out the air. The steaming time will depend on the vat dyes used and can vary from 2 to 5 hr. It will probably be necessary to heat the fabric in the infrared zone to near 100°C. before it enters the chamber.

The experiments with both continuous and Pad-Roll machines on a practical scale are not yet complete. For this reason full details of the process cannot be given. However, the results obtained with the Pad-Roll machine indicate that a commercial process may be expected within a reasonable time.

In principle, any apparatus in which a fabric can be heated to about 100°C. with exclusion of air may be used for the reduction of the dye.

**Oxidation and Soaping**—Oxidation and soaping may be carried out as in normal continuous vat dyeing, but in some cases it will be necessary to use somewhat more acidic solutions and stronger oxidising agents.

#### Appearance of the Dyeings

Although the number of mill-scale dyeings is still insufficient to give full information on the appearance of the dyeings, no special difficulties have been encountered in the dyeing of unmercerised fabrics. With fully continuous dyeing it seems to be difficult to obtain completely speck-free dyeings on mercerised fabrics, a difficulty also encountered in normal pad-steam vat dyeing.

No difficulties with regard to uniformity arose with Pad-Roll dyeings. One of the advantages of this method is the excellent penetration of the fabric (especially if longer steaming times are used),

due to the better migration properties of vat dyes at high temperatures.

The colours of the dyeings may deviate from those obtained in jig-dyeing. The same phenomenon is observed in the high-temperature vat dyeing of yarns.

#### Thermal Stability of the Dyes

Although a number of vat dyes are unstable under the conditions used in the process, many dyes have satisfactory stability, even during the long steaming times used in Pad-Roll dyeings, so practically all colours can be obtained. Some of the less stable dyes can be used if certain auxiliaries, widely used in other high-temperature dyeing processes, are added to the dyebath.

#### Recipes used for Mill-scale Experiments

In order to illustrate the method, some recipes used during mill-scale experiments are given below. For the sake of economy, the quantities of hydrosulphite and formalin added are lower than those given in Fig. 3. The ratios of hydrosulphite to formalin as given in Fig. 3 must be maintained, however, and can be used to obtain the desired potential of the reduction bath when a certain alkali concentration is applied.

		PAD-STEAM DYEINGS (without intermediate drying)	
(a)	2 g.	Fenanthren Brown G disperse powder (G)	
	80 g.	Sodium hydroxide	
	30 g.	Sodium hydrosulphite (80%)	
	25 ml.	Formalin (40%)	
	All per litre.	Steaming time 1 min.	
(b)	11 g.	Fenanthren Brown G disperse powder (G)	
	2.5 g.	Fenanthren Olive T paste new (C.I. Vat Black 25)	
	40 g.	Sodium hydroxide	
	40 g.	Sodium hydrosulphite (80%)	
	17.5 ml.	Formalin (40%)	
	3 g.	Setamol WS (BASF)	
	All per litre.	Steaming time 30 sec.	
		PAD-ROLL DYEINGS	
(a)	30 g.	Indanthren Red FBB powder fine for dyeing, Type 8059 (C.I. Vat Red 10)	
	40 g.	Sodium hydroxide	
	40 g.	Sodium hydrosulphite (80%)	
	22.5 ml.	Formalin (40%)	
	All per litre.	Steaming time 1½ hr.	
(b)	11 g.	Indanthren Brown G powder fine for dyeing, Type 8059	
	2.6 g.	Indanthren Olive MW powder fine for dyeing, Type 8059 (C.I. Vat Green 13)	
	0.9 g.	Indanthren Grey CL powder fine for dyeing, Type 8059 (C.I. Vat Black 31)	
	40 g.	Sodium hydroxide	
	40 g.	Sodium hydrosulphite (80%)	
	26.5 ml.	Formalin (40%)	
	All per litre.	Steaming time 4 hr.	

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HOLLAND

(MS. received 12th May 1959)

### References

- <sup>1</sup> Marshall, W. J., and Speke, R. W., *Teintex*, **19**, 523 (1953).

- <sup>2</sup> Mellbin, B., *Amer. Dyestuff Rep.*, **46**, 770 (1957).
- <sup>3</sup> Eriksson, C. O., Landqvist, N. O., and Mellbin, B. F., *Textil-Rund.*, **10**, 51 (1955).
- <sup>4</sup> Idem, *J.S.D.C.*, **71**, 894 (1955).
- <sup>5</sup> Borsten, H., and van Lamoën, F. L. J., *Tex.*, **14**, 467 (1955).
- <sup>6</sup> Marshall, W. J., and Peters, R. H., *J.S.D.C.*, **69**, 583 (1953).
- <sup>7</sup> Idem, *ibid.*, **68**, 289 (1952).
- <sup>8</sup> Hafenrichter, S., *Melliand Textilber.*, **38**, 1257 (1957).
- <sup>9</sup> Hensel, O., *ibid.*, **35**, 514 (1954).
- <sup>10</sup> *GP* 160,529.

## CORRESPONDENCE

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### Polarography of Azo Dyes

The polarographic reduction half-wave potential,  $E_1$ , is a measure of the ease of reduction. In hydroxyazo compounds the ease of reduction of the azo group is governed by (1) the substituent effect ( $I$ -effect and  $M$ -effect) and (2) the "chelate effect" (based on hydrogen-bond formation between the azo group and the hydroxyl group). According to the electronegativity rule of Shikata and Tachi<sup>1</sup>, electron-releasing ring substituents increase the resistance of the azo group to reduction, and conversely with electron-attracting substituents. The applicability of this rule to azo compounds has been examined by Warwick<sup>2</sup>.

The reduction potentials of solutions ( $5.0 \times 10^{-4}$  mole/litre) of a series of hydroxyazo dyes based on aniline- $\rightarrow$ R acid (2-naphthol-3,6-disulphonic acid) have been measured. Polarograms were determined at 18°C. by means of a recording polarograph (Yanagimoto Co.). Clark-Lubs buffer was used to adjust the pH of the solution, and gelatin was added in order to suppress the maxima. Hydrogen was bubbled through the solution for 10 min. immediately before a measurement was made. The

values of the half-wave potential,  $E_1$ , are given with reference to that of the saturated calomel electrode (taken as zero). The results are illustrated in Fig. 1.

As was suggested by Jaffé<sup>3</sup>, polarographic reduction potentials can be correlated with Hammett's  $\sigma$  values. As is seen in Fig. 1, the results are represented by a straight line with a slope of ca.  $+0.1$  at pH 7.0. The lower the pH, the smaller the slope of the line; the higher the pH, the greater the slope of the line. This relation also holds for a series of azo dyes based on aniline- $\rightarrow$ G acid (2-naphthol-6,8-disulphonic acid).

The polarographic reduction potentials of some water-soluble *o*- and *p*-hydroxyazo dyes were next measured. The results for Orange I (C.I. Acid Orange 20) and Orange II (C.I. Acid Orange 7) are illustrated in Fig. 2. Within the pH range examined, the  $E_1$  values of *p*-hydroxyazo dyes are about 100 mv. more positive than those of corresponding *o*-hydroxyazo dyes.

Mecke and Schmähl<sup>4</sup> have studied the relative reduction rates of a series of azo compounds, using live yeast. They suggested that the stabilising effect of a hydroxyl group *ortho* to an azo group is due to internal hydrogen-bond formation. The observed difference of polarographic reduction potential,  $\Delta E_1$ , between *o*- and *p*-hydroxyazo dyes is due to this "chelate effect"; it apparently

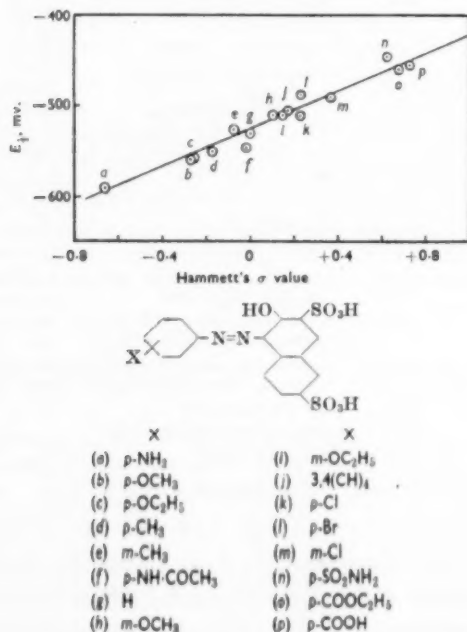


FIG. 1—Relation between  $E_1$  and the Hammett's  $\sigma$  value

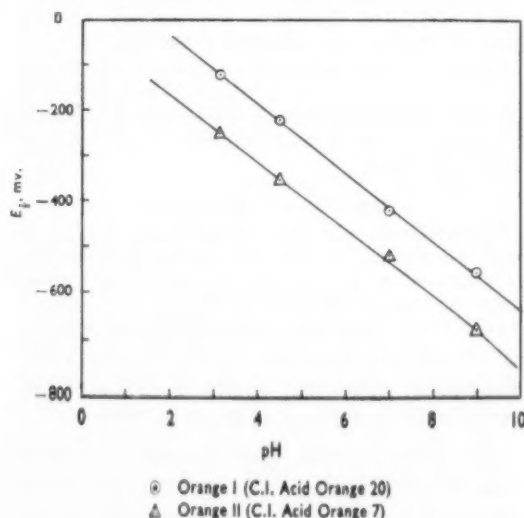


FIG. 2—Relation between  $E_1$  and pH



corresponds to the energy of hydrogen-bond formation between a hydroxyl and an azo group.

Details of the results and a discussion will be published later.

T. IJIMA  
M. SEKIDO

DYEING CHEMISTRY LABORATORY  
TOKYO INSTITUTE OF TECHNOLOGY  
O-OKAYAMA  
MEGURO-KU  
TOKYO  
JAPAN

24th March 1960

<sup>1</sup> Shikata and Tachi, *J. Chem. Soc. Japan*, **53**, 834 (1932).

<sup>2</sup> Warwick, *J.S.D.C.*, **75**, 291 (1959).

<sup>3</sup> Jaffé, *Chem. Rev.*, **53**, 191 (1953).

<sup>4</sup> Mecke and Schmäh, *Naturwiss.*, **42**, 153 (1955).

### The Effect of some Reactive Dyes on the Dimensional Stability of Wool Fibres treated under Stress in Boiling Water

Whewell *et al.*<sup>1</sup> have shown that wool fibres treated for short times in cuprammonium hydroxide neither contract nor take a set when they are steamed under tension.

A similar phenomenon has been observed with carpet-quality, Greek wool fibres dyed with some Procion (Yellow R, Brilliant Red 2B, and Blue 3G) and Cibacron (Yellow R, Brilliant Red 3B, and Blue 3G) reactive dyes, and then treated in boiling distilled water under stress (Fig. 1). The yellow and blue dyes stabilise the structure of the fibres to such an extent as to eliminate contraction almost entirely. However, a set similar to the one obtained with untreated fibres is eventually achieved. The red dyes, which affect the fibre to a lesser extent, do not reduce considerably the maximum supercontraction obtained, but a shift of the peak of the curve towards longer times of boiling is observed; if dyeing is carried out in a more concentrated solution of the dye, and with a larger liquor:wool ratio, the effect becomes more pronounced (Fig. 2).

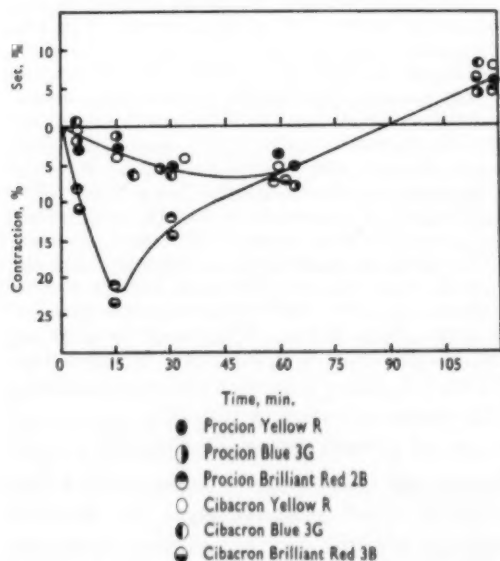


FIG. 1—Effect of Reactive Dyes on the Setting Properties of Wool

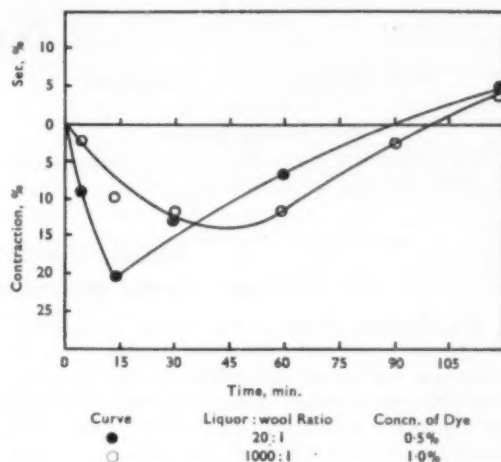


FIG. 2—Effect of the Conditions of Dyeing on the Setting Properties of Wool (Procion Brilliant Red 2B)

Dyeings (10% on the weight of fibre) have been carried out with Procion dyes in the presence of 1% formic acid (85%)<sup>2</sup>, and with Cibacron dyes in the presence of 5% acetic acid and 5% Neovadine AN 200% (Ciba)<sup>3</sup>. Blank experiments to check the effect on the fibre of the assistants, and of the conditions of dyeing, gave the results illustrated in Fig. 3.

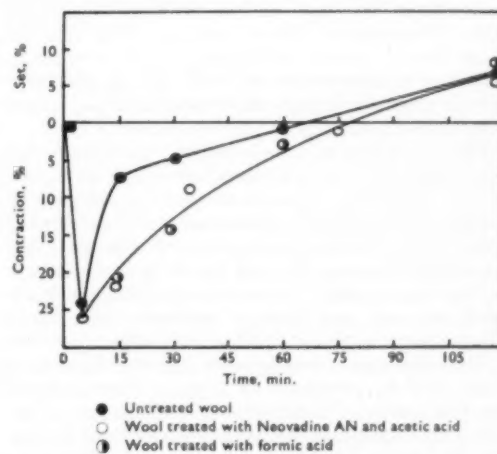


FIG. 3—Effect of (a) Neovadine AN plus Acetic Acid and (b) Formic Acid on the Setting Properties of Wool

This investigation, which is still in progress, was supported by a grant from the Royal Hellenic Research Foundation, to which I am greatly indebted.

A. VASSILIADIS

DEPARTMENT OF INDUSTRIAL CHEMISTRY  
UNIVERSITY OF ATHENS  
ATHENS  
GREECE

26th March 1960

<sup>1</sup> Whewell, C. S., Ashworth, J., Srinivasan, V. R., and Vassiliadis, A., *Text. Research J.*, **29**, 386 (1959).

<sup>2</sup> ICI, *Technical Information Leaflet*, Dyehouse No. 428.

<sup>3</sup> Ciba Review, **11**, (126), 44 (1958).



## Notes

### 250th Meeting of the Committee of the West Riding Section

The Committee of the West Riding Section held its 250th meeting on 24th March 1960.

### Scottish Section

#### Result of the 1960 Junior Essay Competition

The prize of books to the value of three guineas has been won by Mr. W. A. Blue with an essay entitled *Towards Automation in Textile Colouring*.

### British Association of Chemists

#### Hinchley Medal presented to Dr. C. J. T. Cronshaw

The Hinchley Medal of the British Association of Chemists has been presented to Dr. C. J. T. Cronshaw for his great services to the Chemical Industry while head of the Dyestuffs Division of Imperial Chemical Industries Ltd. The presentation took place on the evening of 11th May 1960 at a private ceremony in Dr. Cronshaw's home. It was made by the President of the British Association of Chemists, Mr. J. Wilson, C.B.E., M.C., supported by a Vice-President, Mr.

R. J. Mollard, and the Chairman of the Manchester Section of the Association, Mr. J. Richardson. This presentation to Dr. Cronshaw, who was President of the Society from 1939-1946 and who was elected an Honorary Member in 1947, followed only a few days after the Perkin Medal was presented to him at the Society's Annual Dinner. It must be a source of much gratification and pride to him that the great value of his life's work is being recognised while he is still able to appreciate the honours he has so worthily earned.

### London Section of the Oil and Colour Chemists' Association Twelfth Technical Exhibition

The twelfth technical exhibition organised by the London Section of the Oil and Colour Chemists Association was held at the New Horticultural Hall, Westminster, from 15th to 17th March. There was a record attendance, with a notable influx of overseas visitors, and it was generally agreed that the event this year was even more successful than on previous occasions.

The exhibition essentially provides an opportunity for the demonstration of new advances in raw materials, equipment, and techniques of interest to the oil and colour consuming industries, notably paints and printing inks. It also provides a common meeting ground where the technicians in the consuming industries can discuss such advances and any current problems with their counterparts in the supplying industries.

The exhibition was opened by Sir Alexander Todd, F.R.S., Professor of Organic Chemistry at the University of Cambridge and Chairman of the Advisory Council on Scientific Policy. Both he and the Chairman of the London Section O.C.C.A., Mr. J. A. L. Hawkey, made reference in their addresses to the general lack of scientific and technical manpower and an unusual feature of the exhibition was a Technical Education Stand, organised by four London Technical Colleges, at which advice and information was available to employees and students on educational facilities available in the United Kingdom and the relevant technological qualifications which can be obtained. Twentyone schools sent parties of sixth form students to hear short talks on the paint and printing ink industries.

From the very nature of the exhibition the number of items on display of particular direct interest to the textile chemist was limited. Of

general interest, however, were information and exhibits provided by the Research Association of British Paint Colour and Varnish Manufacturers and by British Titan Products Ltd. on weathering station technique and equipment, including the measurement of sulphur dioxide and other pollution, sunshine, rainfall, temperature, humidity, and ultraviolet intensity. British Titan Products included in their exhibits results of photo-degradation and fading tests carried out on synthetic fibres containing titanium dioxide.

In the organic colour field, Allied Colloids (Bradford) Ltd. introduced two new vat pigments—Paliogen Yellow RT and Paliogen Maroon GR of outstanding fastness properties. Also displayed were their ranges of phthalocyanine pigments and spirit soluble dyes. The Geigy Co. Ltd. introduced the first five members of a new range of multipurpose high quality pigment dispersions, under the name Irgalite MPS colours, suitable for incorporation into both water and oil based systems, and a new flocculation resistant phthalocyanine blue—Irgalite Fast Blue BNF. Golden Valley Colours Ltd. demonstrated how they had extended their range of micronised pigments with a maximum particle size of from 2-5, into the organic field. Imperial Chemical Industries Ltd. introduced a new reddish yellow vat type pigment, Monolite Fast Yellow FRS, with outstanding fastness properties, a new maroon, Monolite Fast Maroon GS, with a yellowish undertone suitable for both opaque and transparent metallic finishes, and a new red pigment, Chromastral Red RS, of good fastness and hiding power. Reeves & Sons Ltd. exhibited their increased range of dispersed pigments available for the colouring of various media. H. Haefner & Co. illustrated the technical

advances made in fluorescent pigments over the last few years, including increased light fastness and brightness, one of their exhibits being an example of a patterned cloth woven from yarn spun dyed by British Celanese Ltd. and having a light fastness of 4-5 on the wool scale. W. Symonds Ltd. illustrated their Hy-D-Sperse ranges of superfine pigment pastes in water.

In the inorganic colour field, Johnson Matthey & Co. Ltd. introduced a new addition to their range, Matthey Titanate Yellow, with outstanding resistance properties to heat, light, and chemical reagents, even when widely extended with titanium dioxide. Laporte Titanium Ltd. presented a product with

similar properties, Titanium Nickel Yellow (C.I. Pigment Yellow 53), prepared by the calcination of titanium and nickel oxides at high temperatures.

Scott Bader Ltd. specifically displayed their Texicote range of polyvinyl acetate emulsions and Texicryl range of acrylic emulsions for textile applications, such as the stiffening, bodying, and bonding of fabrics, the prevention of knot slippage in fishing nets, and in obtaining improved handle. Dunlop also specifically demonstrated a new Polimul emulsion in textile stiffening applications, with high water and humidity resistance and good initial substantivity.

F. R. YOUNG

### Nottingham and District Technical College

A three-year sandwich course (works based) for the College Diploma in Dyeing and Finishing is run by the College. On successful completion of the course for the College Diploma, students may undertake a further year's study which leads to the award of a Higher National Diploma in Applied Chemistry (Dyeing).

A seven-year course leading to the Associateship of the Society of Dyers and Colourists is run for those students who can attend day-release classes in the first five years of the course. At present the final two years of this course are run on an evening basis only.

The College also runs classes leading to City and Guilds of London Institute examinations in dyeing and finishing.

Hostel accommodation is available for full-time students who are not resident within daily travelling distance of the College.

### Chemical Literature

In the American Chemical Society's Official Report 1959 on the Chemical Abstracts Service it is pointed out that the sixth decade of this century saw unprecedentedly strong, accelerated growth in scientific research all over the world. Nearly one million papers reporting new results of chemical and/or chemical engineering research were published, nearly as many in fact as were published in the whole of the four preceding decades. In the eight years 1951-9 the total number of abstracts published each year more than doubled—from 61,074 to 125,440. Of the 125,440 abstracts, 98,680 were of papers and 26,760 of patents. In the section of *Chemical Abstracts* dealing with Dyes and Textile Chemistry there were in 1959 925 abstracts of papers and 1,536 of patents, this preponderance of patents over papers was shown in almost the same ratio in the Paints, Varnishes, Lacquers, and Inks section where the figures were 422 and 661 respectively. This ratio differs widely from that shown in the J.S.D.C. abstracts where in 1959 there were 1,384 abstracts of papers and 1,398 of patents.

### Abstracts of Russian Patents English Translation of the Journal *Biulleten' Izobretenii*

The Russian *Biulleten' izobretenii* is published twice monthly but hitherto no English translation

of it has been available. The need for such a translation has now been met by the publication by Pergamon Press Ltd. of the new monthly journal U.S.S.R. Patents and Inventions. Each number of this journal will contain the abstracts from two issues of the Russian journal. The new journal can be either subscribed for as a whole or for specialised sections of it only. Full particulars are available from Pergamon Press Ltd., 4 and 5 Fitzroy Square, London, W.1.

### Photocopies and Translations of Russian Patents

Pergamon Press Ltd. are now able to supply an authoritative English translation of any Russian patent specification and/or a photographic copy of the original.

### Changes in the British Association's Journal *The Advancement of Science*

A number of changes in the format, content, and frequency of publication are being made as part of the Association's campaign to improve the presentation of science to the public at large. These changes are designed to enhance the journal's appeal to those for whom it is principally intended, viz. scientists who wish to keep in touch with work in fields of study other than their own, students at school and university, and laymen interested in the impact of science on society. The journal is to be published bimonthly and the subscription is £2 per annum.

### The Chemical Society Symposium on Physical, Chemical, and Biological Methods in the Study of High Molecular Weight Carbohydrates Edinburgh 12th-14th July 1960

This symposium will be held in the Edinburgh and East of Scotland College of Agriculture, West Mains Road, Edinburgh 9, in association with the University of Edinburgh on Tuesday, 12th July on Thursday, 14th July 1960. There is a registration fee of £1 15s. 0d. payable by Fellows of the Chemical Society desiring to receive abstracts of the papers or by non-Fellows. The papers presented at the Symposium will not be published in collected form. They deal mainly with polysaccharide chemistry. Full details can be obtained from the General Secretary, The Chemical

Society, Burlington House, London W.1, if application is made before 30th May 1960.

#### **Corday-Morgan Medal and Prize for 1959**

This award, consisting of a Silver Medal and a monetary prize of 200 guineas, is made annually to the chemist of either sex and of British nationality who, in the judgment of the Council of the Chemical Society, has published during the year in question the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the award may be obtained from the General Secretary of the Chemical Society. Applications or recommendations in respect of the award for the year 1959 must be received not later than 31st December 1960, and applications for the award for 1960 are due before the end of 1961.

#### **The Harrison Memorial Prize**

The Selection Committee, consisting of the Presidents of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry, and the Pharmaceutical Society, will, in 1960, consider making an award of the Harrison Memorial Prize.

The prize, which consists of a bronze plaque and a monetary payment of 100 guineas, will be awarded to the chemist of either sex who, being a natural-born British subject and not at the time over thirty years of age, shall, in the opinion of the Selection Committee, during the five years ending 1st December 1959, have conducted the most meritorious and promising original investigations in chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be submitted, should include the full names of the applicant; age (birth certificate to be enclosed); degrees (with name of University); any other qualifications and experience; titles, and reprints if available, of published papers (with co-authors' names); where research was carried out; testimonials and references, and any other relevant particulars.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates who have not attained the age of thirty years at 1st December 1959, and are otherwise eligible for the prize. Any such communication must be received by the President, The Chemical Society, Burlington House, Piccadilly, London W.1, not later than Thursday, 1st September 1960.

#### **Royal Society Scientific Relief Fund**

The Scientific Relief Fund of the Royal Society is available to help scientific men, or their families, as may from time to time require assistance. The regulations governing this fund have been revised and particular attention is drawn to rule 7 which states "Any member of a nationally recognised

scientific society within the British Commonwealth or the Republic of Ireland, acting through one of its officers, may bring cases of need to the attention of the Committee." Sponsors of applicants for relief should obtain confidential information about the applicant's financial situation and apply on the requisite form to be obtained from the Assistant Secretary, Royal Society, Burlington House, London, W.1.

#### **First International Textile Dyestuffs, Finishes and Auxiliaries Exhibition Manchester, 22nd and 23rd September 1960**

This is the first of a new series of annual exhibitions intended to give manufacturers of dyes, finishes, and auxiliary agents a "shop window" for the display of their products. This first of the series will be held in the Free Trade Hall, Peter Street, Manchester, those for 1961 and 1962 in Yorkshire and London respectively.

In addition to the main exhibition in the Free Trade Hall there will be a programme of films in the Lesser Free Trade Hall (both halls are in the same building) and on one day there will be a symposium on new developments in textile chemicals.

Further particulars can be obtained from the organisers, Clarke & Rhodes Ltd., 274-276 The Corn Exchange, Manchester.

#### **XXXII<sup>e</sup> Congrès International de Chimie Industrielle Barcelona, 23rd-30th October 1960**

This congress, which is being held for the fourth time in Spain, will have sections dealing with rubber and plastics; pigments, paints, and inks; paper; textiles; leather; and organic chemistry. Offers to present papers are welcomed and those desiring to do so should apply for the necessary form to the Comité Scientifique et Technique du XXXII<sup>e</sup> Congrès International de Chimie Industrielle, Cámara Oficial de la Industria, Ancha II, Barcelona 2, Spain, to whom also requests for further details regarding the congress should be addressed.

#### **Second Canadian Textile Conference**

The Second Canadian Textile Conference sponsored by the Textile Technical Federation of Canada and the Primary Textiles Institute will be held in the Queen Elizabeth Hotel, Montreal, on 7th, 8th, and 9th February 1961. Full details regarding the conference, in which all sections of the industry will take part, can be obtained from Primary Textiles Institute, 630 LaGauchetière St. West, Montreal, Que., Canada.

#### **Meetings of Council and Committees May**

Council—4th  
Colour Index Editorial Board—13th  
Publications—17th  
Diplomas—17th  
Disperse Dyes Subcommittee—27th

## OBITUARY NOTICES

**William Graham**

William Graham, Chairman of the Northern Ireland Section of the Society, died on 27th February 1960, at the age of 52 years.

Mr. Graham received his initial training in textile dyeing at York Street Flax Spinning Co. Ltd. and the College of Technology, Belfast. Further technical education was acquired at the Department of Colour Chemistry and Dyeing of the University of Leeds.



He then became dyehouse manager at Wm. Clark and Sons Ltd., where he worked until 1944, when he became a director of John Hanna Ltd. Under his influence and ability this firm soon became one of the leading commission dyers and finishers in Northern Ireland, and it was no surprise that he soon became managing director, the position he held at the time of his death.

Mr. Graham joined the Society at the time of the formation of the Northern Ireland Section in 1946. He became a committee member in 1954 and served in this capacity until 1957, when he was elected Vice-chairman. After two years' Vice-chairmanship he was elected Chairman in March 1959, and would have held this office for a further two years had he survived. He had an implicit belief in the Society and all that it stood for. He scarcely ever missed a lecture or committee meeting, and his enthusiastic support for all our functions—whether technical or social—was always forthcoming.

Rugby Union football, gardening, and photography were the hobbies pursued by Mr. Graham. He was a committee member of Ballymena Rugby Football Club. In gardening his special hobby was grafting, and it was quite a pleasure to see the results of these experiments in his admirable garden. In recent years he became an expert photographer, and his pictures won prizes in open competition.

Bill Graham was an admirable fellow in every way. He had a most congenial disposition and an ever ready sense of humour, which made knowing him a pleasure. His passing has left sorrow in the hearts of a very wide circle of friends whose privilege it was to know him well.

He was a devoted family man and leaves a widow and three daughters.

JAMES PORTER

**Benjamin William Marchant**

We regret to record the death on 9th January 1960, at the age of 74, of B. W. Marchant.

A native of Stroud, he received his early education at Marling School and after winning a Clothworkers Scholarship, studied at Leeds University.

On leaving the University he was employed for some time as chemist with T. and F. Firth and Sons Ltd., and later went to the Mannheim works of B.A.S.F.

During the first world war he was a chemist on the T.N.T. plant of Chance and Hunt of Oldbury (Birmingham).

In 1919 he joined the firm of C. Roberts and Co. Ltd. (then agents for J. R. Geigy) and later the Geigy Co. Ltd. as a technical and sales representative, with whom he remained till his retirement.

In his younger days he was a keen sportsman and at the University gained many honours at Rugby, athletics and swimming. He played Rugby with Headingley and the old Horton Club, which later became the present Bradford R.U.F.C. of which he was a founder member. He served as President of the Bradford club in the seasons 1933-34 and 1934-35. He was selected to play for Yorkshire against Lancashire in 1912.

"Benny" Marchant, as he was known to his friends, was a well known figure in the trade in Yorkshire, the West Country, and the Kidderminster area. He attended meetings regularly and was a frequent contributor to the discussions.

He is survived by a widow.

A. E. BATTLE

**Eric Thornton**

Eric Thornton died at the tragically early age of 43 years on 4th March 1960. Educated at Huddersfield College and University of Leeds, where he gained a B.Sc. in Colour Chemistry and Dyeing, he joined the Yorkshire Dyeware and Chemical Co. Ltd. immediately after graduation. After some early work on anthraquinonoid disperse dyes he became a plant chemist and soon found himself more at home in the works than at the bench. At the time of his death he was head of the Anthraquinone Department at the Kirkstall Road Works of the Yorkshire Dyeware & Chemical Co. Ltd. where he had worked continuously since his appointment as Research Chemist in 1938.

He gained his Soccer colours at Leeds University, played once for the Combined Universities and up to the start of the illness which led to his death



he played regularly for the Huddersfield Old Collegians. He was a great reader with a leaning towards books of a historical nature. A quiet man, he always enjoyed the talk and company of small groups of his friends and colleagues, whether this was over a glass of beer or while walking the hills. The cynicism with which he occasionally expressed himself did not conceal from those who knew him a fine sense of fairness and a steadfast loyalty.

Always approachable he was ready at all times to listen to and learn from the views of his junior colleagues.

He was an abstractor to the Society, regularly attended the meetings of the West Riding Section, and had served as a part-time lecturer in chemistry to Leeds College of Technology for many years. He leaves a widow and a daughter.

R. K. FOURNESS

## New Books and Publications

### Review of Textile Progress

Volume 10, 1958

Manchester and Bradford: The Textile Institute and the Society of Dyers and Colourists; London: Butterworths Scientific Publications. 1959. Pp. 494. Price, 50s. 0d.

The publication of Volume 10 of the Review marks a change in that the name of Butterworths Scientific Publications Ltd. appears as joint publisher with the Textile Institute and the Society of Dyers and Colourists.

In the Foreword the Chairman of the Joint Committee, Mr. G. S. J. White, expresses the hope that the new arrangements will ensure that the Review appears more promptly and that it will become self-sustaining, a hope that all readers will share.

This volume follows lines similar to that of its predecessors, but some changes are promised for the second decade. The Review is divided into 11 sections which are further divided into sub-sections. The 34 contributors, including one from France and one from America, deal first with the science of fibres, then consider their conversion into yarns and fabrics, and finally their dyeing and finishing. There are also sections on colouring matters, analysis and testing, laundering and dry-cleaning, building and engineering and, finally, a section on the industrial applications of textiles.

The field covered is immense and the contributors have examined some 3,300 original papers or patents. With such a coverage compressed into a moderately sized volume it is obvious that the treatment has to be less complete than one would wish, but this should not be taken as a criticism of the contributors who, presumably, have had to work within closely set limits. It does, however, raise the question considered in some detail by the reviewer of the two previous volumes\* whether the present pattern is the best. This is a difficult question, and the answer will vary from reader to reader. The research worker in a particular field with modest library facilities, possibly even only the Journals of the Textile Institute and the Society of Dyers and Colourists, will have read more detailed abstracts on his subject long before the Review appears, and will have made his own assessment of the material. The present volume will, however, still be valuable to him over a wider field, and especially valuable to those, not directly

engaged in research, who wish to keep abreast of modern developments, and to anyone who requires a useful reference volume.

The reviewer must confess, however, to a longing for a more critical assessment of the more important evidence of the year, or possibly for this to be done for one or two sections, say every five years, while maintaining a condensed series of references to papers so as to complete the coverage. Possibly this is "crying for the moon" when papers are published at the rate they are, but we lay a heavy burden upon our children by this multiplicity of papers, many of which, alas, contain little really new material. Such sentiments may be the cry of one who has to read too much.

A work of this nature does not lend itself to detailed review, but careful reading of sections of especial interest indicates that the coverage is good and the brief comment accurate. It was a little arresting, however, to read about raw wool scouring under the section "Finishing Wool Fabrics", and perhaps a more general title might have been chosen for this section. The review is well printed and reasonably priced, and readers will endorse the words on the dust cover: "A concise guide to textile research, expertly edited, thoroughly indexed". It is a "must" for workers in textiles and it reflects great credit on the members of the joint committee of the Textile Institute and the Society of Dyers and Colourists. Warm thanks are due to the contributors for their efforts which, as the reviewer knows from personal experience, are in effect a labour of love.

J. BARRITT

### Précis des Matières Colorantes Synthétiques Tome I—Matières premières et produits intermédiaires

By Henri Wahl. Pp. iv + 339. Paris: Presses Universitaires de France. 1958. Price, 2,400 francs.

This volume is the first of a set of three, Volume II of which was published three years ago (J.S.D.C. 74 (1958) 307), the third one will deal with dyeing and printing. I contains a systematic survey of the raw materials and their extraction from coal tar and from oil. This is then followed by chapters dealing separately with the different unit processes employed in the manufacture of intermediates. A short appendix deals adequately with the electronic theory of aromatic substitution.

A. JOHNSON

\* Speakman, P. T., J.S.D.C., 74, 586 (1958), and 75, 462 (1959)





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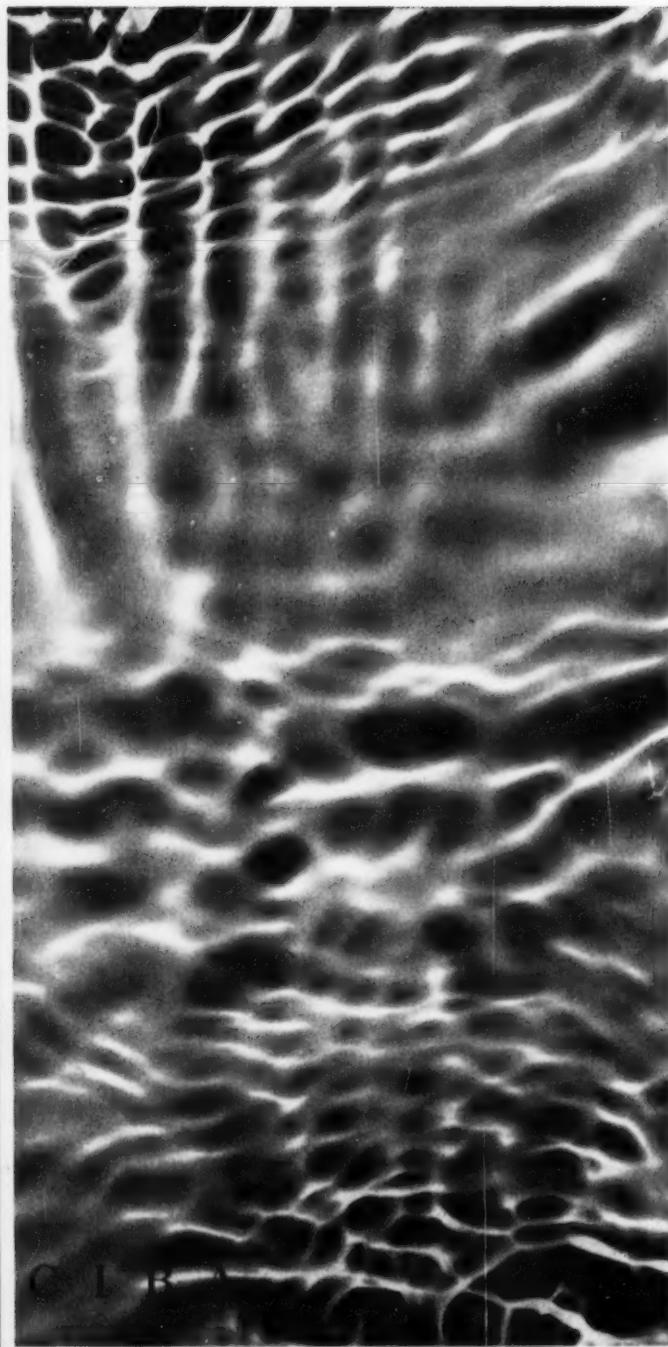
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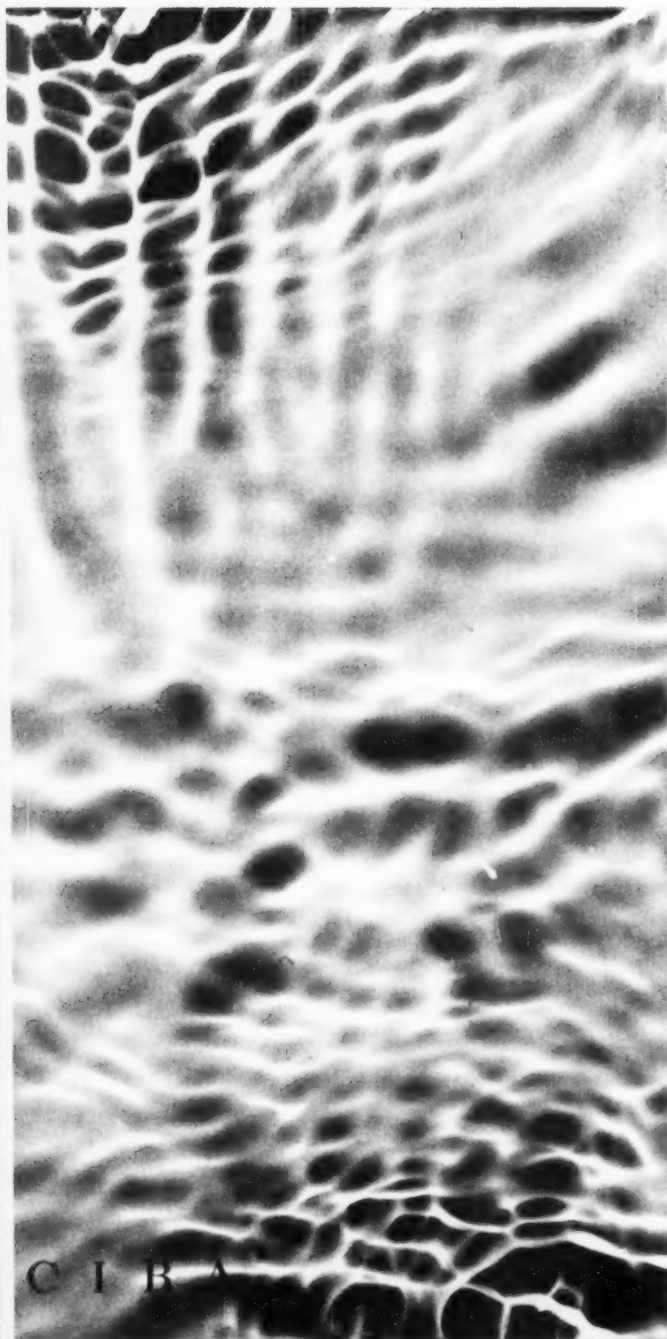
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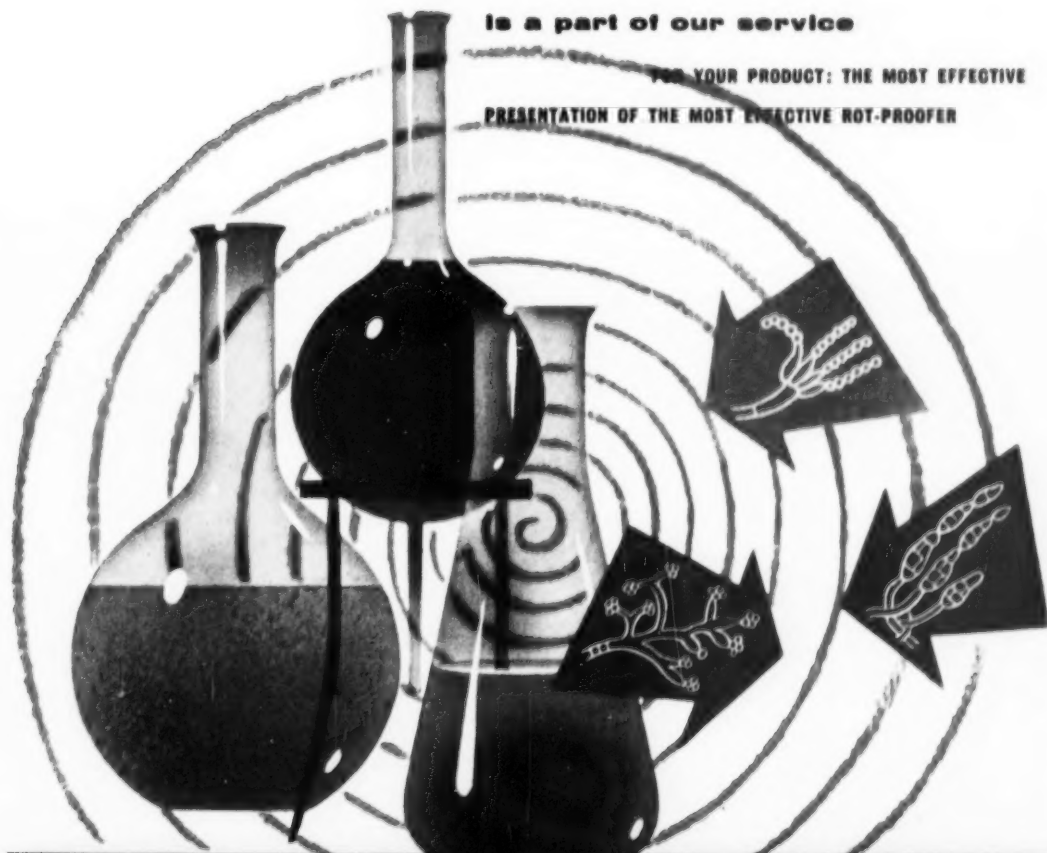




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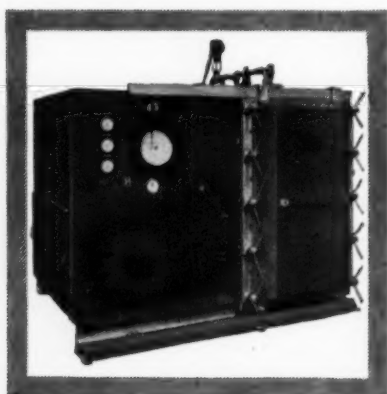
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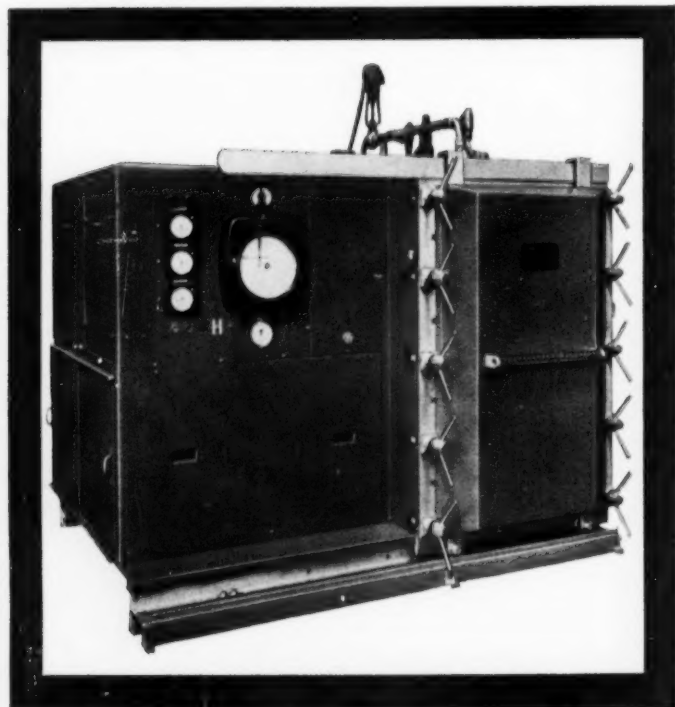
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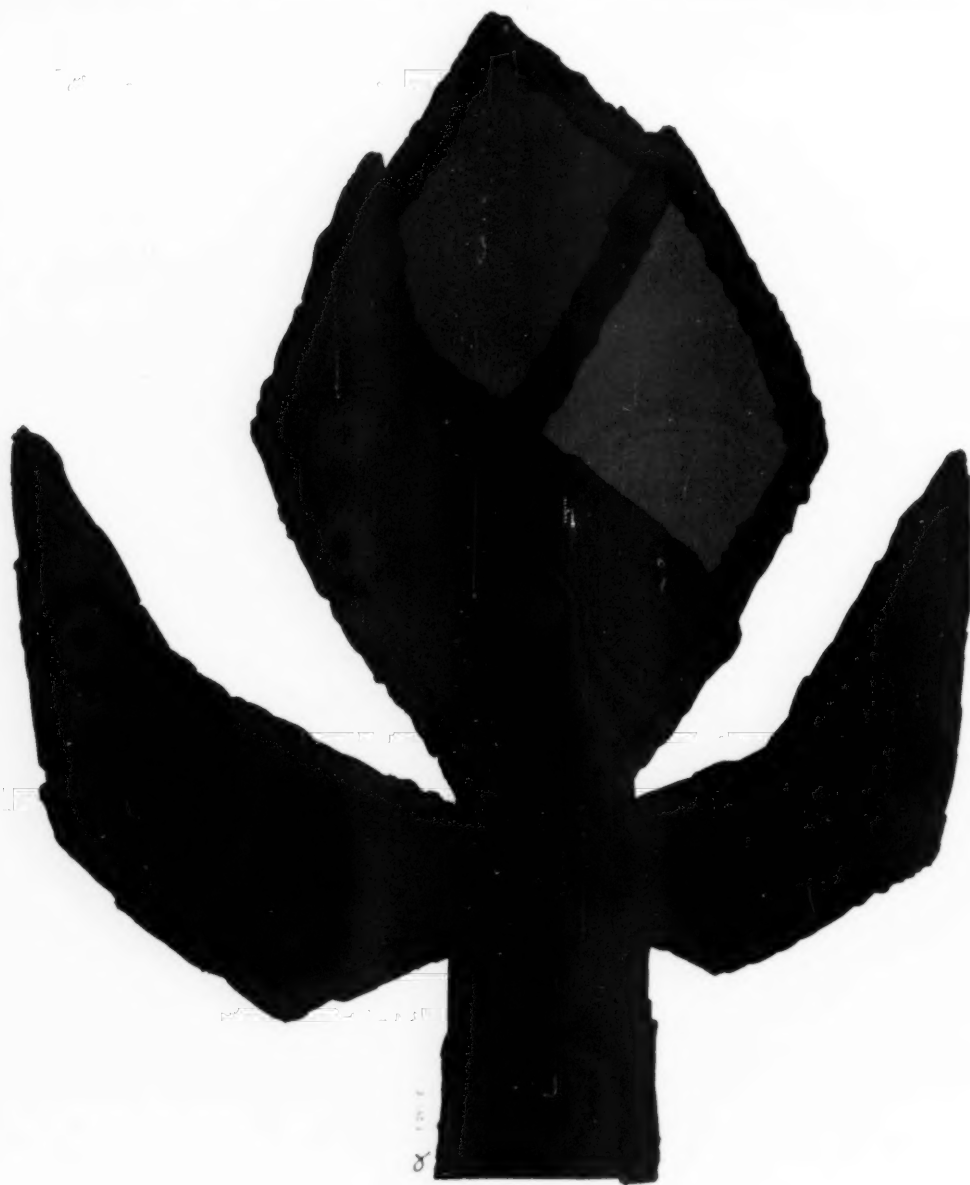
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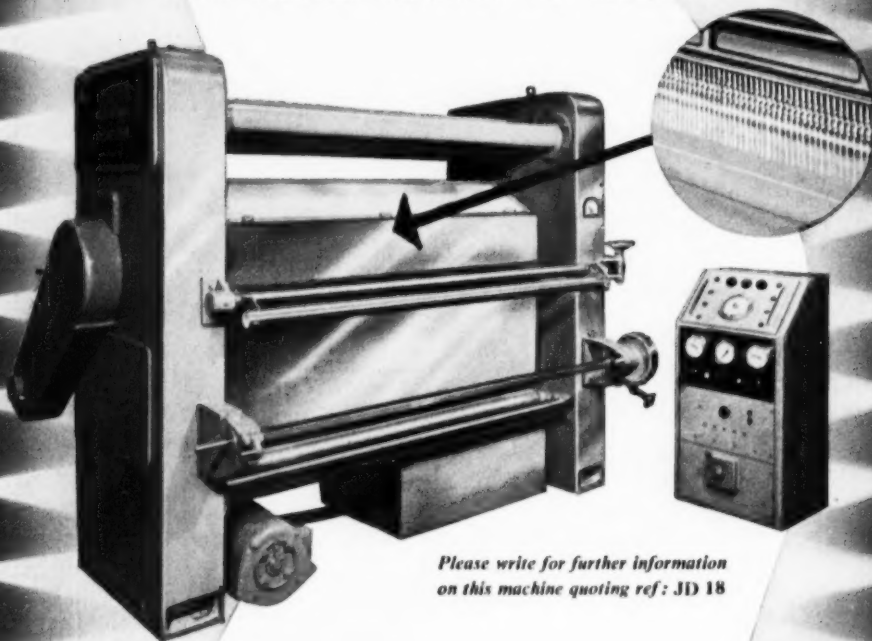
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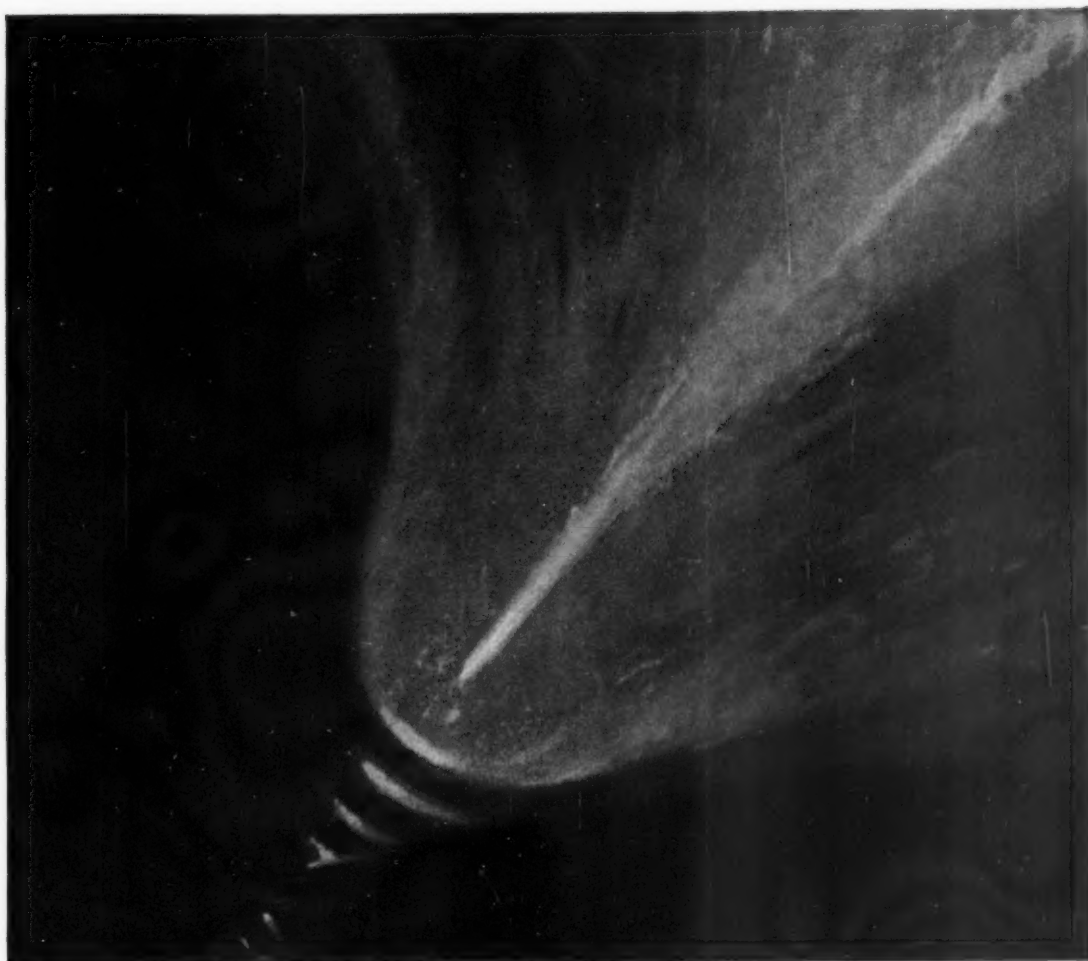
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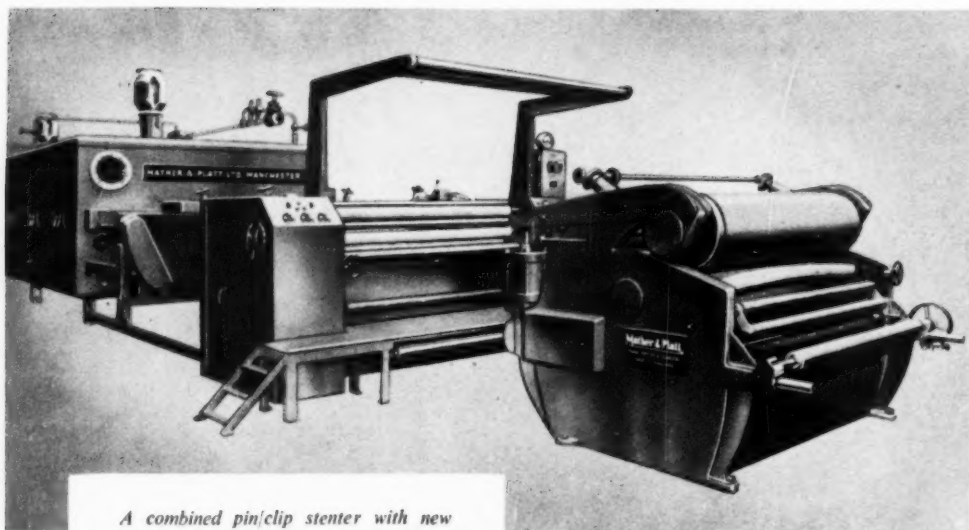
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### Künstliche organische Farbstoffe und ihre Anwendungen

By W. Seidenfaden. Pp. vii + 256. Stuttgart: Ferdinand Enke Verlag. 1957. Price, DM 44.50 (Paper DM 42.00).

Inevitably this book will be compared with that of Professor Wahl, published at about the same time, and much the same might be said about them both.

Seidenfaden's text is also an accurate and methodical survey of the methods of preparation and the general chemical properties of the different groups of dyes, classified according to their chemical structure. Perhaps too much has been attempted in the space available; to dismiss colour and constitution in three pages is altogether too trivial.

To deal with phthalocyanines in only five pages is a more serious curtailment.

Above all else, this book is a catalogue following the classical tradition of textbooks on dye chemistry. But the emphasis is changing; the dye-chemist is devoting more of his attention to the behaviour of his compounds in use as dyes on textile and other substrates. It would be a welcome change to see this reflected in a textbook.

A. JOHNSON

### Man-made Textile Encyclopedia

Edited by J. J. Press. Pp. xiv + 913. New York and London: Textile Book Publishers Inc. A Division of Interscience Publishers Inc. 1959. Price, £10 (\$27.50).

To review this encyclopedia both critically and in detail would require at least a dozen reviewers and a disproportionate share of the *Journal*. Alternatively it could, perhaps, be dealt with briefly by saying that it is a mine of information which should be available in all libraries—private individuals may understandably be reluctant to pay £10 for a book, however good.

Man-made textiles are surveyed from raw materials to marketing methods, production statistics, and registered trade marks. The scheme of presentation is by processes, as far as possible in logical sequence; arrangement is by fibres within certain of the chapters. Covering as it does the entire manufacturing field the information is somewhat generalised and superficial, a limitation more than counterbalanced by the preferential treatment given to newer processes. A great deal of the material is not easily come by; thus, there are 8 pages (approx. 800 words per page) on ropes and cordage and about 30 pages are devoted to industrial fabrics such as belts, tyre cords, hosepipes, filter cloths and fabrics for reinforced plastics. Also worth particular mention are the sections on high-bulk yarn processing, identification of warp sizings, sewing threads, tufted carpets, laces and nets, non-woven textiles, fibres in paper-making, cloth cutting machines, stitching and associated problems of distortion and stability, domestic and commercial laundering, and dry cleaning. The text is very well illustrated by photographs, line drawings and process flow diagrams. Outstanding in this respect is Section 8

of Chapter XIII where 54 graphs are included in the 20 pages devoted to a most useful summary of data on the effect of blending on fabric performance.

It is probable that the main value of the book will be as a source of general information in fields that are outside the reader's own speciality. Certainly it is doubtful if the dyeing and finishing sections will be of great interest to specialists in these subjects. An outline of the principles, methods and machines for dyeing and printing (11 pages) is followed by accounts of pigmented emulsion dyeing and printing (3 pages) and the dyeing of special fabrics such as pile fabrics, carpets, upholstery and lace (2 pages). The dyeing of individual fibres and blends is dealt with fibre by fibre (23 pages), each section including preparation (such as scouring, bleaching, and stripping), the dyes suitable for that fibre and methods for dyeing the fibre in blends. An example of the generalised approach is provided by the statement, unqualified, that azoics give a good white discharge with hydrosulphite print paste. A further 5 pages are occupied by 21 examples of specific routines, which in turn is followed by 5 pages on flock printing.

Finishing (21 pages) is divided into four sections, mechanical treatments, chemical treatments, specific finishes for non-blended fabrics, and coated fabrics, and includes a useful tabulated summary of chemical finishes. This chapter does not adequately emphasise the growing importance and complexity of chemical finishes, and a most serious omission is the absence of a section on flameproofing, which, particularly in view of current interest, could well have been given considerable emphasis.

Chapters likely to be of limited interest outside the U.S.A. are those on Performance Standards (22 pages), Marketing (72 pages), and Statistics, as these are written largely in relation to the American industry.

J. W. BELL

### Die Prüfung der Textilien

Edited by H. Sommer and assisted by F. Winkler. Being the 5th Volume of Handbuch der Werkstoffprüfung. Zweite Auflage. Edited by E. Siebel. Pp. xxx + 1,440. Berlin: Springer-Verlag. 1960. Price, DM 225.00.

This volume is the textile section of a German national "standard work" embracing the testing of those materials utilised by mankind for his various needs. The last example of this type, in the textile field, was the work of Heermann and Herzog entitled "Mikroskopische und mechanisch-technische Textiluntersuchungen", the last edition of which appeared in 1931, and is now out of print.

In view of the vast and rapid development in textile testing methods and equipment since that time, and particularly during the last decade, it has been found necessary to completely review and reorganise the system of presentation, rather than to attempt to build merely upon the previous foundations. In fact, one of the greatest drawbacks to the production of an up-to-date work of this type has been this rapid and continuing advancement and multiplicity of methods which



could easily result in certain sections being out of date by the time of actual publication. The publishers are therefore to be commended for their enterprise and courage in undertaking this task. In spite of these drawbacks the success of this work has been assured from its very inception because it has had the collaboration of the German State Testing and Research Institutions, the various Technical Institutes and the Trade. Including the editors, twenty-two authors of national and international reputation, each a specialist in his own branch of the subject, have contributed in a concerted team effort to produce an all embracing system which could be accepted as a "standard work" which, even allowing for continued extension of this subject, could stand as a basis for many years to come.

As would naturally be expected of a "standard work", the matter is presented in a systematised form. The volume commences with a 37 page introduction outlining the modern conceptions of fibre science. The remainder is divided into four main parts, as follows—1st part, Optical investigations; 2nd part, Mechanical-technological investigations; 3rd part, Textile-chemical investigations; 4th part, Textile serviceability tests.

These four parts are composed of a total of twenty sections and these sections are divided into numerous subsections. The clearly set-out table of contents together with the usual type of index renders finding of any subsection quite simple. A rough estimate indicates that the literature references are well above the three thousand mark

and are suitably placed at the end of each chapter or section. Their extent can be taken as a measure of the efforts made by the respective authors to supplement and confirm the results of their personal experiences.

Though no claims are made that the work covers every possible method of test to which textiles are subjected, the reader will find very little that has been left out, even though the field is very broad, from X-ray and electron-microscopy to actual wear and field trials under varied climatic conditions.

The print is of excellent quality and the general production leaves nothing to be desired. The illustrations are of that quality which one expects of a first-class publication, and, even where actual photographs of testing apparatus are shown, they are usually accompanied by those sensible line drawings illustrating the basic principles involved, a method of presentation which is a usual feature of modern German publications.

The size and price of the book, together with the fact that it is published in German, will naturally result in a limited sale in this country; it should, however, find a prominent place on the shelves of every technical library which claims to serve the textile trade, as well as in the bookcase of every progressive firm interested in the production or conversion of textile materials. To the serious student, to whom the price is not out of the question, this book could be recommended with the assurance that his money would be well spent.

J. WOOD

#### New Books received

- Symposium on Microscopy*, S.T.P. 257. Philadelphia: American Society for Testing Materials, 1959. Pp. vi + 165 + 1 colour plate. \$4.75.
- Symposium on Light Microscopy*, S.P. 143. Philadelphia: American Society for Testing Materials, 1953. Pp. vi + 126. \$2.50.
- Separation and Identification of Food Colour Permitted by the Colouring Matters in Food Regulations 1957*. London: Association of Public Analysts, 1960. Pp. vi + 31 + ii half-tones. 21s. 6d. (postage 9d.).
- Titles of Periodicals from the U.S.S.R. and "Cover-to-Cover" Translations*. London: Department of Scientific and Industrial Research, Lending Library Unit, March 1960. Pp. iii + 82. No price.
- Time Study Manual for the Textile Industry*. NORBERT LLOYD ENRICK. New York: Textile Book Publishers Inc., a division of Interscience Publishers Inc. 1960. Pp. vii + 216. 49s. 6d.
- Moisture in Textiles*. J. W. S. HEARLE and R. H. PETERS (editors). Manchester and London: Textile Institute and Butterworths Scientific Publishers, 1960. Pp. ix + 203. 40s. 6d. (1s. 6d. postage). (\$6.50).
- The Chemistry of Heterocyclic Compounds, Volume XIV. Pyridine and its Derivatives—Part I*. ERWIN KLINGBERG (editor). R. A. BARNES, F. BRODY, and F. R. RUBY (contributors). London and New York: Interscience Publishers Inc. 1960. Pp. x + 613. 367s. 6d. for the 4 Parts (subscription 315s. 6d.).
- Chemical Analysis of Resin-based Coating Materials*. C. P. A. KAPPELMEIER (editor). London and New York: Interscience Publishers, 1959. Pp. xxvii + 630. 147s. 6d. (\$19.50).
- Methoden der Organischen Chemie* (Houben-Weyl). Band V, Teil 4, Halogenverbindungen. E. MÜLLER (editor). 4th edition 1960. Stuttgart: Georg Thieme Verlag. Pp. xlviii + 894. DM 180.00.
- Introduction to Colloid Chemistry*. KAROL J. MYRSELS. London and New York: Interscience Publishers, 1959. Pp. xv + 475. 75s. 6d.
- Handbuch für Textilingenieure und Textilpraktiker*. Fachteil T61—Grundlagen der Textilveredlung. M. PETER, 8th edition 1960. Wuppertal-Elberfeld: Dr. Spohr-Verlag. Pp. xi + 413 including adverts. DM 10.80.
- The Analysis of Fatty Acids and Fatty Alcohols*. Technical Publication No. 6. New Ferry, near Birkenhead: Price's (Bromborough) Ltd. March 1960. Pp. 149. Gratis.
- Handbuch der Werkstoffprüfung*. Zweite Auflage. Band V. Die Prüfung der Textilien. H. SOMMER, assisted by F. WINKLER (editors). 2nd edition 1960. Berlin-Wilmersdorf: Springer-Verlag. Pp. xxxi + 1,440. DM 225.00.
- Review of Textile Progress, Volume 10, 1958*. Manchester, Bradford, London: The Textile Institute, The Society of Dyers and Colourists, and Butterworths Scientific Publications, 1959. Pp. 494. 50s. 6d.

## Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes.  
Any publication abstracted may be referred to by members of the Society on application to  
Dr. C. B. Stevens, Dyeing Department, Leeds University

### Ciba Clayton Ltd.

**CIBALAN DYES APPLIED AT HIGH TEMPERATURES ON COURTELLE**—This card contains dyeings in two depths on Courtele sliver of twenty-four 2:1 dye:metal complex dyes from the Cibalan range using the high temperature method based on BP 777,534 (Kunstzidespinnerij Nyma NV—assignors to Courtaulds Ltd.) in which the dyebath is set with 10 g./l. sodium sulphate (or other electrolytes) at 50°C., the temperature raised to 125–130°C. during 35–40 min. and dyeing continued for 60 min. at this temp. Exhaustion of certain dyes is promoted by adding 1% of glacial acetic acid. Build-up to navies and blacks is possible and the dyeings have very good fastness to light and wet treatments. Thus a 6% dyeing of Cibalan Navy Blue RL and a 15% dyeing of Cibalan Black 2BL both have a fastness of 7–8 to light, 4 to mechanical washing A and 4 to alkaline milling.

### Ciba Ltd.

**CIBA REVIEWS NOS. 134, 135 AND 136**—No. 134 is devoted to physical testing and includes articles on (1) the history of textile testing, (2) the aims, problems and limitations of physical testing, (3) basic problems and methods of testing, and (4) physical testing for the finisher. The technical section deals with one-bath methods for dyeing acrylic fibre, cellulosic fibre mixtures; improving the wet fastness of dyeings and prints and the dyeing of woolled sheepskins with level-dyeing acid dyes, reactive dyes, Cibalans and Neolans (after chlorination) and with selected direct and leather dyes to dye the leather and reserve the wool.

No. 135 describes the rise and development of the textile trade in and around Rouen and contains the expected wealth of information and illustrations. The technical section includes information on the levelling action of Univadine W when dyeing chlorinated wool with acid-milling dyes; the clearing of the disperse dye stain from the wool portion of wool-polyester fibre mixtures; and the effect of resin finishes on the light fastness of Cibacron dyeings and prints. In addition there is a description of trichromatic printing using Cibacron dyes with emulsion thickenings. It is claimed that a great variety of attractive colour combinations, primarily suited for use on dress goods, blouse materials and squares, can be obtained. There is also a further note on the Eidophor system of colour and black and white television developed by GRETAG, an affiliate of CIBA Ltd.

No. 136 describes Peruvian textile techniques. The technical section includes information on the production of pastel colours by a new one-binder Microfix process; one-bath methods for dyeing acrylic fibre-wool mixtures using Univadine W; and the prevention of the soiling of tufted carpets with Antisoiling TC.

### J. R. Geigy A.G.

**SOLOPHENYL GREY A3BL: SOLOPHENYL GREY ABL**—This direct dye gives dyeings of good fastness to light and stability to resin finishing. Wet fastness is very good in pale depths and often adequate in medium depths without aftertreatment. They both belong to Group B of the S.D.C. classification but in spite of their high rate of exhaustion and low migrating power level dyeings can easily be obtained by salt control. High solubility and rapid fixation make them very suitable for pad-dyeing. They are of interest for direct printing and dyed grounds are readily dischargeable. Fastness figures on viscose include—

	Light	Washing a (40°C.)	Perspiration
Grey A3BL	6-7	4	3-4
Grey ABL	6-7	3-4	3

**SOLOPHENYL GREY A3BL**—This card describes the same dye as the previous card. It has been issued because

Solophenyl Grey ABL also described in the previous card is not available in Great Britain.

### The Geigy Co. Ltd.

**IRGA-SOLVENT PROCESS FOR NYLON**—This leaflet describes a method of applying acid dyes to nylon on the jig using benzyl alcohol, 4% v/v., and Irgasol NJ, an anionic auxiliary product, to promote the uptake of dye and uniformity of coverage on continuous filament material. It is claimed that a wide range of colours of all depths are possible with excellent reproducibility from laboratory matching to bulk and from batch to batch, and a higher rate of production than previously obtainable. The fastness of dyeings to washing is considerably greater than that obtained with disperse dyes.

**IRGA-SOLVENT PROCESS FOR WOOL**—This leaflet outlines a method for dyeing loose wool and slubbing with neutral-dyeing metal complex dyes and selected fast-to-milling acid dyes using benzyl alcohol, 2–4% on volume of dyebath, to promote the rate of uptake of dye whereby satisfactory exhaustion is obtained after dyeing for about 30 min. at 80–60°C. Brighter dyeings, improved condition of the wool and saving in labour and other costs are claimed.

### L. B. Holliday & Co. Ltd.

**MONOCHROME BLUE RB**—This chrome dye gives navies of very good fastness to light and wet treatments on wool, being particularly recommended for application by the single-bath method. It is also of interest, dyed after-chrome, on silk, nylon and Acrilan. Owing to its low solubility in cold water, dyeing should commence at 70°C. No ammonia or other alkali should be present when dissolving and Glauber's salt should not be added when dyeing after-chrome. Dyeings are dischargeable to white. Fastness figures on wool include—Light (in full navy) 7–8, alkaline milling 4.

**PARADONE PRINTING BLACKS TL-(F) AND BL-(F)**—These two indigol vat dyes are specifically intended for printing cellulosic materials to give greys and blacks of excellent fastness to light. Printed by the potash Ernsol C method, fixation is uniform over a wide range of conditions and it is possible to store for reasonable times between printing and steaming if draughts and acid fumes are excluded. Prints should not be exposed to direct sunlight between steaming and washing. They are supplied as non-settling, non-freezing pastes—SF Paste conc. (F) in the title indicates the "FELISOL" designation. Fastness figures on cotton, for both dyes, include—Light 6, chlorine 5, washing 5.

**SUPREXCEL BLUE 4RL**—This class A direct dye gives royal blues of good fastness to light on all types of cellulosic material. It is very level dyeing with maximum affinity at 60–80°C. It is also suitable for dyeing the cellulosic component in cellulosic-protein fibre mixtures and for direct printing. Dyed grounds are dischargeable to white. In the non-textile field it is of interest for dyeing full-chrome and vegetable tanned leathers and sulphite paper pulps. Fastness figures on cotton include—Light 5–6, washing (S.D.C. Test 2), perspiration 2.

**DYES FOR WOOL AND WOOL MIXTURES**—This monograph (140 pp.) gives a comprehensive account of the dyeing behaviour, fastness properties and uses of all the ranges of wool dyes, supplemented as necessary with details of types of dyes and methods for colouring mixtures of wool with cellulosic fibres, silk, polyamides, polyesters and acrylics, including Acrilan. There are also summaries of wool scouring, carbonising and bleaching, notes on water and on the use of Ferrolons A and B for sequestering metal ions and on the common procedures for dyeing loose wool, slubbing, yarn and cloth.

### Farbenfabriken Bayer

**CONTINUOUS DYEING**—This book (58 pp.) describes continuous dyeing methods, using steaming for fixation, for applying vat, direct, aftercoppered direct, diazotised

and developed direct and coupled direct dyes to cellulosic materials. Thirty-four patterns are included, taken from large-scale dyeings of all these types of dyes. Complete procedural details are given in each case.

**ISOLAN BORDEAUX BBLS**—This 2:1 dye:metal complex dye is recommended for dyeing all forms of wool and polyamide fibres, its very good solubility and levelling power making it very suitable for application in circulating-liquor machines. It is also of interest in dyeing wool-cellulosic fibre mixtures and silk and for Vigoureux printing. Fastness figures on wool include—Light 7, washing b (140°F.) 4-5, milling b 4-5.

**ISOLAN RED 3GLS:ISOLAN RED GLSN**—These two 2:1 dye:metal complex dyes give yellowish reds and slightly bluish reds, respectively, when dyed on wool. They have good solubility and levelling power and are recommended for use, alone and in mixtures with other members of this range, for dyeing all forms of wool and polyamide fibres. They are also of interest on silk and wool-cellulosic fibre mixtures and for Vigoureux printing. Fastness figures on wool include—

	Light	Washing b (140°F.)	Milling b
Red 3GLS	6	4-5	4
Red GLSN	6	4-5	4

**NAPTOL AS ON STAPLE FIBRE YARN**—This card contains dyeings in two depths on spun bright viscose rayon staple yarn of 223 different azoic combinations, grouped according to the coupling component, 29 of which are used, plus one combination, AS-SG + AS-SR, giving a black. Notable features are the range and brilliance of colour displayed and the large number (73) of combinations given the Indanthren label of fastness. It is pointed out that Naphtol AS combinations on viscose rayons are distinguished, as a rule, by their level-dyeing behaviour, even in pale depths, and their high fastness to light compared with that of dyeings on cotton make them suitable for pale to medium depth dyeings on this fibre. Data for quantities of coupling and diazo components and figures for fastness to light, chlorine, chlorite, peroxide and ironing are appended alongside each set of patterns.

**NAPTOL AS ON COTTON YARN**—This card describes "a selection of important Naphtol AS combinations on cotton yarn which are distinguished by their all-round fastness properties". It contains dyeings in two depths of no less than 318 combinations, all the yellows and pale colours being on bleached yarn and the others on unbleached, boiled-out yarn. Combinations are grouped according to the coupling component used (30, plus one mixture, AS-SG + AS-SR), these in turn being arranged in order of substantivity. The largest number of diazo components used with any one Naphtol is 31 (with AS-SW). The dyeings have been produced by impregnating in the beck at 30°C. for 30 min., hydro extracting and developing in the beck cold for 30 min. 99 combinations may be designated with the Indanthren fastness label, provided the requirements are observed regarding the minimum depth of colour prescribed for the relevant field of application. In this connection it is noteworthy that all the combinations (11) based on Naphtol AS-KG may be so labelled, having a fastness (in full depth) of 6-7 or better to light and 4 or better (in all except two instances) to chlorine and peroxide bleaching. This card, which is of the loose-leaf type, is a very fine production.

**PHTHALOGEN DYE STUFFS**—This card describes the "M" range of Phthalogen dyes which consists of 6 members, the original green, turquoise and blue being supplemented by Blue IRM, Navy Blue IRRM and Blue Black NM. The metal is already incorporated in the Phthalogen dye and only a solvent, Levasol PO, P or F, and ammonia need be added to the printing paste, development of the insoluble metal-complex being brought about either by steaming for 5-10 min. in neutral or acid steam, or by dry heat for 5-8 min. at 130-140°C., followed by acidification to remove unfixed metal compound. The Phthalogen M dyes may be mixed together in all proportions. The fastness properties of the prints obtained on cellulosic fibres are remarkable. Fastness to light at 1/4th standard depth is not less than 7 and in standard depth is 8 in all cases. Fastness to all

other agencies, including the most severe (except chlorine) is not less than 4-5. Fastness to chlorine (a) is from 3 to 4 and to chlorine (b) 2 to 3. In addition to the usual patterns, the card includes samples of multi-coloured prints showing the use of Phthalogen M dyes alongside Rapidogens and Anthrasols. The Indanthren label may, of course, be given to a wide variety of prints based on every one of these dyes.

**PHTHALOGEN BRILLIANT BLUE IF3GK:PHTHALOGEN TURQUOISE IFBK:PHTHALOFIX FN FOR YARN DYEING**—This card describes the use of Phthalofix FN which simplifies earlier dyeing procedures for dyeing cellulosic fibre yarns and gives better fastness to rubbing. The method consists essentially of pretreating the material at 80°C. for 45 min. in a solution of Phthalofix FN, dyeing cold for 20-30 min. with the Phthalogen dye, and developing the insoluble phthalocyanine pigment inside the fibre by treating the "dye" material in a caustic soda/sodium hydrosulphite solution at 50°C. for 15 min. (Turquoise is best developed in zinc sulphoxylate-formaldehyde-formic acid.) A method for dyeing silk is also included. In this case pretreatment with Phthalofix FN is unnecessary and development of the insoluble pigment is brought about by treating in sodium hydrosulphite solution acidified with formic acid. Both dyes give dyeings having fastness 7 to light and 4 or better to all other agencies except chlorine and sodium chlorite bleaching.

**ASTRAZON AND ASTRA DYE STUFFS FOR DRALON: CATIONIC DYES FOR ACRYLIC FIBRES: PARTS I AND II**—These two cards contain dyeings in five depths on spun Dralon acrylic fibre of 35 Astrazon dyes and five Astra dyes. They are intended for dyeing all types of acrylic fibres, the Astrazon "L" brands (19) being preferred where high light fastness is required in pale depths, the remaining dyes reserved for medium to full depths. All give dyeings of good fastness to wet treatments. They are applied from neutral or weakly acid dyebaths in presence of a cationic levelling agent, e.g. Levagal PAN. Attention is drawn to the importance of the saturation value of each acrylic fibre and the saturation value for each dye on Dralon is given together with its "saturation factor" which is useful for determining whether the total amount of dye used in a particular mixture is within the limit for complete exhaustion to be obtained and "blocking" to be avoided. The time of half-dyeing of each dye, dyed to the same depth (approx. half standard depth) in presence and absence of Levagal PAN, is also given. The colour range is complete and a range of 63 mixture dyeings illustrates the possibilities of colour mixing. Even at high dyeing temperatures the migrating power of these dyes is very poor and it is essential to obtain initial uniform uptake by temperature control and the use of restraining agents. Dyeing may be carried out at 105-108°C. and this is essential in the case of continuous filament material when medium to full depth dyeings are required. Such high temperature dyeing is unsuitable for "high bulk" yarns. Addition to the dyebath of Persofast WKF is particularly recommended with the latter whereby dyeing, softening and antistatic treatment is possible in one operation.

**AXIL C**—An aliphatic amide for use as an activator in chlorite bleaching when using impregnation methods. It is not suitable for use in long liquors.

**BLANKOPHOR BE**—A fluorescent brightening agent primarily intended for use on cellulosic materials and having very good levelling properties and thus very suitable for application in circulating-liquor machines working at short liquor:material ratios. It is also suitable for use in peroxide bleach baths, and is of interest on polyamide fibres and mixtures of them and cellulosic fibres.

**PERLIT D PREPARE:PERLIT D SALT**—Perlit D Prepare is a cationic paraffin emulsion and Perlit D Salt is a trivalent chromium complex dissolved in isopropyl alcohol and the two are used together for water-repellent finishes on cellulosic and synthetic fibres.

**BAYER COLORIST. No. 9**—This issue contains articles on the production of white and coloured matt prints with Acramin products, cloth dyeing with Acramin dyes, direct printing on Dralon muslin with basic and disperse dyes and the finishing of simplex goods (imitation doeskin leather gloving materials made of cotton, spun viscose rayon and, more recently, polyamide fibres).



**Farbwerk Hoechst A.G.**

**SAMARON DYE STUFFS ON TREVIRA**—These are a range of disperse dyes suitable for dyeing polyester fibres. The card contains dyeings in three depths (except for blacks) on Trevira cloth (the polyester fibre manufactured by Hoechst) heat set for 30 sec. at 200°C. before dyeing and dyed at 100°C. in presence of Remol TRF as carrier, except in four cases where dyeing was carried out at 120°C. In all cases a "reduction-clear" is recommended using hydrosulphite and caustic soda with the addition of Leomine HSG, except for cloth where Hostapal CV or Hostaphat LN3 is recommended. The text includes full details of dyeing procedures, notes on dye selection and methods for dyeing blends of Trevira and wool on cellulosic fibres. Fastness figures are included for both carrier-dyed and high temperature-dyed material.

**SCREEN PRINTS WITH RAPID FAST AND RAPIDAZOL DYE STUFFS**—This card contains prints on bleached, mercerised cotton cloth of 24 Rapid Fast and three Rapidazol dyes together with nine multicoloured prints produced with combinations of these dyes and solubilised vats and Remazol reactive dyes. It is noteworthy that prints of fourteen dyes, designated by an "I", may be given the "Indanthren" fastness label.

**RAPIDAZOL DYES**—This card describes the properties and uses of five new members of the Rapidazol range of mixtures of azo coupling components and stabilised diazo compounds for printing cellulosic fibres, viz. Bordeaux R, Violet B, Blue MB, Green B, and Brown IR. They can be developed by neutral steaming. Rapidazol Violet B and Blue MB require the presence of an activator under neutral steaming conditions and Rapidazol Salt M has been introduced for this purpose. The use of these dyes in conjunction with the Remazol reactive dyes is particularly recommended and the card contains nine prints of this type.

**Imperial Chemical Industries Ltd.**

**TECHNICAL INFORMATION LEAFLETS—Dyehouse No. 544. Printing of Secondary Cellulose Acetate**—The printing behaviour of Procilyn, vat and disperse dyes is summarised, typical recipes given and the fastness properties of representative ranges of dyes of each type are tabulated.

**Dyehouse No. 547. Effect of the Si-Ro-Set Method of Durable Pleating on Dyes Applied to Acrilan, Silk, Nylon, Terylene, Secondary Cellulose Acetate Rayon and Triacetate Rayon**—The change of hue, staining of adjacent material, etc. occurring when dyeings on the appropriate fibres were given the Si-Ro-Set treatment and followed by the heat setting processes, are tabulated. It was noted that (1) thioglycolic acid does not, in general, affect the hue and staining behaviour of disperse dyes on secondary cellulose acetate rayon, although there is considerable delustering of the fibre; (2) there is no change in hue or staining of disperse dyes on triacetate and, in general, no change in hue or staining of these dyes on Terylene and nylon; (3) the majority of dyes examined on silk and Acrilan possess very good fastness to heat treatments and moderate to good fastness to the Si-Ro-Set process, except vats and solubilised vats which possess excellent fastness to it. Since the degree of marking-off usually increases with increasing depth of colour, it is suggested that where staining is important the susceptibility of the dyes at the depth to be used be determined under the particular conditions of treatment to be used.

**Dyehouse No. 548. The Printing of Nylon**—The behaviour of Procynyls, Nylomines, acid dyes and disperse dyes when printed on nylon is summarised. Typical recipes are given together with notes on the use of mixtures and tabulated fastness data.

**Dyehouse No. 549. The Printing of Triacetate Rayon and Triacetate/Viscose Rayon Blends**—The behaviour of Procynyls, disperse dyes and vat dyes (applied by both the alkali-leuco ("all-in") and the acid leuco process) when printed on triacetate rayon is summarised. Typical recipes are given and tabulated fastness data.

**Dyehouse No. 551. Printing of "Terylene" Polyester Fibre**—Selected disperse dyes are recommended. Fixation is achieved by either steaming or dry heat. Using the steaming method, Tumesal PH is necessary for the production of deep colours. Addition of Resist Salt L to

the print paste is recommended when fixing in steam or by dry heat. With dry heat the minimum temperature should be 180°C. for economic running and fixation is complete in 60 sec. at this temperature or in 40 sec. at 200°C. The range of dyes suitable for dry heat fixation is limited by their volatility. Ten dyes are recommended. The effect of steaming time, steam pressure and Tumesal PH on build-up when using steam fixation is also tabulated.

**METHIC FAST PAPER BLUE 6G**—This homogeneous basic dye gives brilliant greenish blues of high light fastness on paper. It is very soluble and is suitable for all types of surface coloration as well as for beater dyeing. It also has high resistance to acids, alkalis, and hypochlorite. It has high affinity for bleached cellulose and excellent backwaters are obtained even in absence of sizing materials. Fastness figures for a dyeing on bleached sulphite pulp S.R. 40° sized with 2% rosin, 4% alum, include—Light 5, sulphuric acid 5, bleach (0.4% available chlorine) 4-5.

**PROCION BRILLIANT ORANGE 2R**—This reactive dye is suitable for printing cellulosic fibres using both steaming and non-steaming methods and gives bright reddish oranges of good fastness to light and wet treatments. Fastness figures on cotton include—Light (Bombay) 4, hypochlorite ("dry-chemicking") 3-4, washing (Test No. 5, five times at 100°C.) 4-5.

**PROCION BRILLIANT YELLOW H3G**—This reactive dye gives bright greenish yellows of good fastness to light and washing when printed on cellulosic fibres and builds up well to golden yellows. Print paste stability is excellent and even at full depth the washing properties of the print paste are good. It is also of interest for bright greens in combination with the blues in the Procion "H" range. Fastness figures on cotton include—Light (xenon arc) 6, washing (Test No. 5, five times at 100°C.) 5.

**PROCION SCARLET HR**—This reactive dye gives bright scarlets when printed on cellulosic fibres, building up well to full depths. Printing pastes have very good stability. It is also of interest for printing silk and chlorinated wool. Fastness figures on cotton include—Light (Wilmslow) 4, hypochlorite (dry-chemicking) 3-4, washing (Test No. 5, five times at 100°C.) 4-5.

**FLUOLITE MP LIQUID**—This fluorescent brightening agent is of particular interest to the paper industry for whitening sized and unsized finishes by adding to either the beater or machine chest, for surface whitening by aftertreatment and for improving the whiteness of coating mixes. Information is provided on the factors affecting the whitening power of Fluolite MP.

**MIGRATION INHIBITOR V**—This is an anionic organic "polyelectrolyte" designed to inhibit or reduce the migration of colour during the drying of cloth padded with aqueous solutions or dispersions. It is of particular interest when padding dispersions of vat dyes, where padding is followed by drying. It is also of interest with Procion dyes, particularly when applied by the pad-dry-pad-steam process, and also with direct dyes of low affinity applied by a pad-dry process. It is recommended as an anti-migration agent when dyeing synthetic fibres by pad-dry techniques, particularly when using disperse dyes and vat dye pigments. It is marketed as a straw-coloured, moderately viscous liquid which has an alkaline reaction. 2-10 g./litre of padding liquor are required. Coloured plates illustrate the effect of adding 5 g./l. of the product on pigment migration using Caledon Brilliant Red 3B and Caledon Olive Green B.

**Sandoz A.G.**

**DRIMARENE-Y REACTIVE DYES FOR PRINTS ON CELLULOSIC FIBRES**—This card describes a range of 11 reactive dyes for pad-dyeing cellulosic fibres. They are very soluble, have only slight substantivity even in presence of electrolytes and dye not chemically combined with the fibre is easily removed. Padding liquors are prepared containing urea, sodium carbonate, and thickening, as required. These are stable for 24 hr. at room temp. and for several hours at elevated temperatures. Fixation may be by dry heat or steam heat. The colour range includes yellow, orange, scarlet, crimson, violet, blue (including turquoise), grey, and black. Compared with the Drimarene-Z range for printing, there is no equivalent to Yellow Z-3GL or Blue Z-GL but Scarlet

Y-GL and Red Y-RL, in their turn, have no equivalents in the Drimarene-Z range. The card also contains greys produced with Black Y-BL and 10 mixture dyeings produced by the dry heat fixation method. Each dye is shown on mercerised cotton sateen (3 depths), cotton gabardine and spun viscose rayon, all dyeings fixed by dry heat, and on bleached cotton overprinted with Black Z-BL and fixed by steaming. The light fastness of dyeings ranges from good to very good and fastness to severe washing is excellent.

PALETTE No. 3.—This issue is largely devoted to colour photography and includes the following articles. "Possibilities and Limits of Colour Photography" by E. Scheidegger; "Colour Photos" by Suzanne Hausammann; "Coloured Night. Underwater Landscape and Colour Perception" by H. Haas; "Organic Chemistry and Colour Photography" by A. van Dornael; and "Colour and Molecular Structure; Part II" by C. Gastellu. There is also an article, "The Role of Fibre Microstructure in Textile Finishing" by E. Elod.

## Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index

### I—PLANT; MACHINERY; BUILDINGS

#### Chemical and Mechanical Deterioration of Wood in Contact with Iron

J. E. Marian and A. Wissing

#### II—Chemical Decomposition

*Svensk Papperstidning*, 63 (29 Feb 1960) 98-106  
(in English)

Chemical examination of rusted and non-rusted wood including cross-ties, 10 years in the track, confirmed the hypothesis that contact with rusting iron mainly affects the holocellulose portion of wood, involving degradation of hemi-cellulose into NaOH-soluble products. A theory is presented explaining the decomposition of polysaccharides in wood as metal-catalysed autoxidative chain reactions. 15 references.

#### III—Effect of Some Wood Preservatives

*Ibid.*, (15 March 1960) 130-132 (in English)

Scots pine was treated with creosote and with zinc-chromium arsenate and subjected to the effects of rusting iron as described earlier (*ibid.*, 63 (15 Feb 1960) 47-57; J.S.D.C., 76 (May 1960) 305). Creosote showed some beneficial effect, especially in tensile strength. Zinc-chromium on the other hand promoted decomposition by rusting iron. The results are, however, not conclusive as the treated samples were not identical with the untreated samples. It would appear that preservatives do not prevent chemical changes in wood in contact with rusting iron.

#### IV—Prevention of Deterioration

*Ibid.*, (31 March 1960) 174-183 (in English)

Experiments with galvanising, hot-dipping, resin treating, anti-oxidant impregnation, and cathodic protection are reported. Most satisfactory results were obtained by galvanising the iron or by applying a water-resistant synthetic resin coating. Results with anti-oxidants and cathodic protection were erratic suggesting that either the wooden material was more susceptible than earlier samples or that there was a deteriorating effect by electrical currents. R.A.

#### PATENTS

#### Dyeing Tow of Synthetic Polymers

H. K. Houser

USP 2,904,954

A hollow bobbin on which the tow is wound and is dyed by dye liquor passed from the bobbin through the tow. The tow is dried on the bobbin and then processed into yarn. This enables production of dyed yarns which are as elastic as undyed yarns. C.O.C.

#### Treating Web Materials with Liquids or Gases

Patex Corp.

USP 2,904,981

Apparatus in which cloth, paper, warps, etc. are passed through a liquid or gas which is subjected to agitation or vibration at 5-60,000 cycles per sec. Thus the cloth passes between opposed rigid walls one of which at least has a row or rows of transducers close to one another. These transducers set up ultrasonic waves in the liquid or gas and these waves vibrate through a rapid succession of changes in dimension and transmit these vibrations as pressure waves to the liquid or gas. C.O.C.

#### Fluid Bed Machine for Drying Filaments, Threads, etc.

British Rayon Research Assocn.

BP 817,992

Describes a fluid bed machine for the continuous drying of yarn. C.O.C.

#### Wet-processing of Textile Webs

B. Kawaguchi

BP 828,236

The web is led into and through a vat containing the processing liquor. It is guided through the liquor by means including a roller around which the web passes. The roller has a hollow shaft running through it and bearings which maintain it coaxial with but apart from the shaft. The roller is below the level of the liquor. The shaft has at least one opening in it and its hollow interior is connected to a suction device. The roller is perforated so that the liquor can be drawn through the web and roller into the hollow shaft. C.O.C.

#### Sonic to Ultrasonic Vibrations for Increasing Penetration of Liquid into Textiles

H. A. Poole and F. W. Bellows

BP 829,296

The vibrations are set up by a source, e.g. a transducer, totally immersed either in the processing liquor or in an electrically non-conducting liquor which isolates the source from the treating liquid. C.O.C.

#### Coating with Flock, Tinsel or the like

D. & S. Processing Co.

USP 2,903,376

Apparatus in which the sheet being coated is caused to vibrate by treatment with sonic or supersonic compression waves during coating. This avoids use of mechanical beaters and offers improved control of the coating. C.O.C.

#### Screen Printing Cylinders

A. J. C. de Oliveira

BP 830,506

Modification of BP 756,315 (J.S.D.C., 72 (1956) 613). The metal mesh after the pattern has been applied to it is given an electrically conductive coating on one or both sides of the impermeable areas. It is then electroplated which results in the meshes becoming welded together resulting in the impermeable areas becoming coated with a coherent layer of metal without however closing up the permeable areas. C.O.C.

#### Turning and Trimming Hose

B. P. Hall (Textiles)

BP 831,136

Vertical forms mounted on arms pivoted to an axle carried by a work table are used for turning and for carrying seamless hose during cutting, i.e. trimming of floating threads on the inside of the hose. Hose are first turned, then as the form moves round the table a retractable rod within the form is raised by a cam plate on the table to engage the toe pocket during the cutting operation. G.F.K.

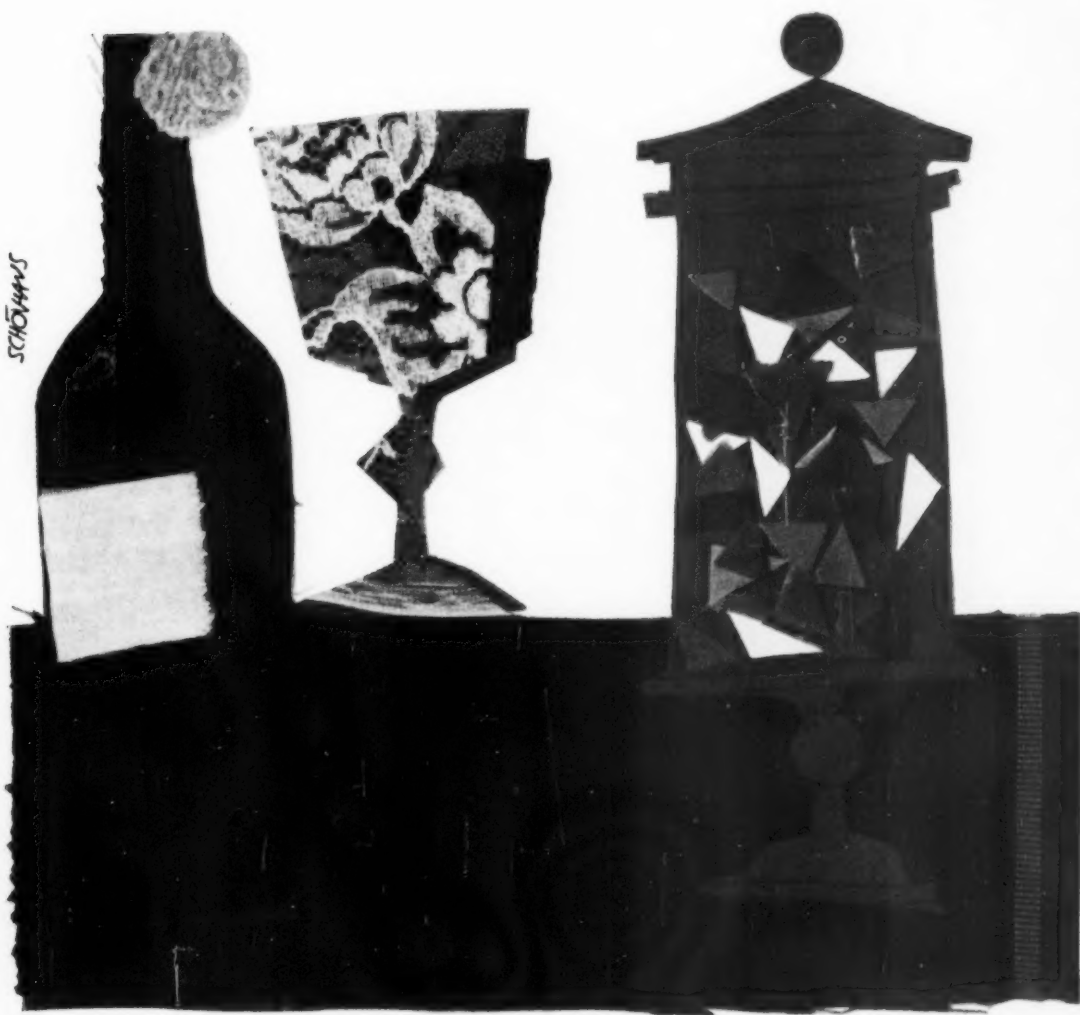
#### Continuous Calendaring of Thermosetting Resins

Montecatini Società Generale per l'Industria Mineraria e Chimica

BP 831,917

A pair of rollers rotating at different speeds and in opposite directions is mounted with a third roller placed above the faster of the two rollers and rotating in the opposite direction to it. This third roller has projections in the form of a helicoidal spiral, the edges of which abut the roller beneath it. The sheet of resinous material





**Reactive dyestuffs**

**for printing cellulosic fibres**

**Details overleaf**



**® Drimarene-z**

**SANDOZ PRODUCTS LTD BRADFORD**

# <sup>®</sup> Drimarene-z

Reactive dyestuffs  
for printing  
cellulosic fibres

## 9 Important features

- Bright shades
- Simple method of application
- All brands suitable for combination
- Excellent stability of the printing pastes
- Perfect reproducibility of shade
- Stable chemical linkage with the fibre
- Very good stability to steam
- Unreacted dyestuff readily removed by washing
- Excellent wet fastness

The range of **Drimarene-z** dyestuffs comprises at present

Drimarene Yellow Z-4GL\*  
Drimarene Yellow Z-3GL\*  
Drimarene Orange Z-G\*  
Drimarene Red Z-2B\*  
Drimarene Violet Z-RL\*  
Drimarene Blue Z-RL\*  
Drimarene Blue Z-GL\*  
Drimarene Turquoise Z-G\*  
Drimarene Navy Z-BL\*  
Drimarene Grey Z-GL\*  
Drimarene Black Z-BL\*

<sup>®</sup> Registered trade mark of SANDOZ LTD

\* Patent applied for



SANDOZ PRODUCTS LTD BRADFORD

formed on the faster roller as the resin, etc. is fed in between the first two rollers is cut by the edges of the projections and simultaneously turned over and moved along the roller. This yields a very homogeneous product. C.O.C.

**Automatic Silk Screen Printing of Ceramics**  
J. V. Fernandez BP 832,650

## II—WATER AND EFFLUENTS

### PATENTS

**Mechanical Screens for Waste Liquors**  
Longwood Engineering Co. BP 818,111

**Treatment of Wool Scouring Effluent**  
U.S. Secretary of Agriculture USP 2,903,424

Adding colloidal bentonite at the same time that the effluent is acidified results in a much larger proportion of the grease being separated and the resulting clarified liquor has a considerably lower B.O.D. C.O.C.

## III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

### Rôle of Cationic Group in Anionic Detergents

M. Kashiwagi and H. Ezaki

*Bull. Chem. Soc. Japan*, 32 (June 1959) 624-626  
Organic salts of dodecyl sulphate, including triethanolamine dodecyl sulphate, morpholine, pyridine, have been compared with Na dodecylsulphate from the viewpoints of surface chemistry and bulk properties. There was no difference in surface area when adsorbed on conc. ammonium sulphate. Critical micelle concn., determined by surface tension and foaming power, were also similar. Viscosity and solubility of these organic salts differed considerably when compared with Na salt. Similar results were obtained with triethanolamine alkyl benzene sulphonate when compared with the Na salt. Apparently the cationic group changes bulk properties but not the surfactant properties. F.J.

### The Cellulosic Solvent Cadoxen, Its Preparation and Viscosimetric Relationship with Cupriethylenediamine

D. Henley

*Swensk Papperstidning*, 63 (15 March 1960) 143-146 (in English)

The solubility of high D.P. cellulose in cadoxen, a cadmium ethylene diamine hydroxide complex, depends on the Cd concn. High solvating powers are obtained with 4.5-5.2% Cd (by wt.) and 0.2-0.5 M NaOH. To 963 g. of 117-118°C. fraction of dist. 76% aqueous ethylene diamine (80% ethylene diamine) 1,780 g. H<sub>2</sub>O and 270 g. CdO were added and the mixture was shaken for 24 hr. at 3°C. The supernatant liquid was resaturated and 40 g. solid NaOH were added to 2.5 l. of soln. which after centrifuging at room temp. contained 5-6% Cd. When preparing a cellulose soln. it is advisable to wet the cellulose with a few drops of H<sub>2</sub>O before dissolution in order to swell the fibres and prevent gel formation. Comparison of the intrinsic viscosities of a series of cellulose samples in cadoxen and in Cuen showed a linear relationship:  $\eta$  in cadoxen  $\times$  1.23 =  $\eta$  in Cuen for sample of any molecular heterogeneity. R.A.

### Hydrogen Bonding and Properties of Starch

M. I. Knyaginichev and Yu. R. Bolkhovitin

*Doklady Akad. Nauk S.S.S.R.*, 126 (11 June 1959) 1129-1131

Specimens of natural and modified (treatment with 2 N-H<sub>2</sub>SO<sub>4</sub> for 4-7 days at room temp.) starch show an almost identical absorption band in the infrared (2.8-3.1  $\mu$ ), characteristic of hydrogen bonding, but differ considerably in viscosity. It appears therefore that hydrogen bonding alone is not responsible for the physical properties of starch. G.J.K.

### Carubin and Guar—Vegetable Binders and Thickeners

A. Lukaszczyk *Textil-Rund.*, 15 (March 1960) 130-134

After some introductory remarks concerning the occurrence of the trees from which the two gums are produced the chemistry of carubin and guaran are discussed. Both are polysaccharides. Carubin consists of 80-84% mannose and 16-20% d-galactose, guaran of 65% mannose and 35% galactose. Guar is soluble in cold water, carubin is not. On addition of alkali the viscosity

of the solutions of either substance decreases slightly at first. Further addition of alkali causes marked increase of viscosity and then flocculation. Neutral salts of mono- and divalent metals have no effect on aqueous solutions of carubin and guaran. Small amounts of tannic acid, Fehling-solution, phosphotungstic acid and lead acetate cause precipitation. It is assumed that complex formation is responsible for this reaction. Carubin and guaran can be crosslinked with the aid of formaldehyde or epichlorohydrin. Ester and ether derivatives of carubin and guaran are known but up till now only the carboxymethyl- and the hydroxyethyl- and hydroxy-propylethers are of practical interest. In conclusion the technical application of the two gums is discussed. Apart from the textile industry they are used in the paper and food industries, for flotation, in the ceramic industry, in the oil industry and most recently for the detoxication of effluents. W.M.

### New Thickeners for the Textile Industry

W. Porges *Textil-Rund.*, 15 (March 1960) 126-130

After discussing the requirements a thickener has to fulfil and the progress made in this field the author describes a new thickener obtained by etherification of carubin (locust bean gum) and recently put on the market under the name of Meypro Gum CR. This is readily soluble in cold water and stable to alkalis. It can be coagulated, however, by borax. The suitability of this thickener for different printing styles and especially for the "Colloresin" process is discussed. In this connection a new quick-acting reducing agent Rongal A (BASF) is mentioned. Another brand, Meypro Gum KN (not etherified), is coagulated by alkalis and is especially recommended for use on Brenthol-prepared goods. W.M.

### PATENTS

### Bactericidal Detergent

General Mills

BP 830,880

Germicidally active quaternary ammonium compounds form mixtures, soluble to stable clear solutions in water, with anionic surfactants of formula  $RNH(CH_2CH_2COOX)$  or  $RN(CH_2CH_2COOX)_2$  ( $R$  = aliphatic hydrocarbon of 8-22 C;  $X$  = cation). Thus a mixture of lauryl dimethyl benzyl ammonium chloride and sodium coco  $\beta$ -amino-propionate yields a clear solution in water. The solution is stable to long standing and the quaternary compound's bactericidal properties are unaffected by presence of the propionate. C.O.C.

### Dry Lubricants for Use in Lace Making

W. J. & T. Lambert & Co.

BP 817,003

A mixture of 70-95% of graphite and 30-5% of an anionic surfactant is an excellent dry lubricant for use on lace making machines or the like, e.g. for dusting on the bobbin guides and carriages. Any stains formed on the lace are readily removed during normal wet processing. C.O.C.

### Dye Stripping Solution

Rohm & Haas Co.

USP 2,902,453

When stripping dyes with a reducing agent presence of 0.5-4.0% on the weight of the fibres of a compound of formula  $R^1R^2R^3R^4NA$  (at least one of  $R^1, R^2, R^3, R^4$  = aliphatic, arylaliphatic or alicyclicaliphatic of  $> 7$  C and any others = Alk of 1-7 C, allyl, benzyl, phenoxyethoxy-ethyl, hexahydrobenzyl, etc.;  $A$  = anion), e.g. (methyl-dodecylbenzyl) trimethylammonium chloride, results in much more efficient stripping. C.O.C.

### Dry Compositions yielding Cationic Melamine Resin Solutions when Dissolved in Water

Ciba

BP 830,620

A dry mixture of melamine hydrochloride (0.5-1.0 mol. HCl per mol. melamine) and a methylol melamine capable of forming a hardenable melamine resin with the hydrochloride, e.g. hexamethylol melamine, is soluble in water. The solution retains its usefulness even when aged at 60°C. for 200 hr. C.O.C.

### Resinous Water-repellent Agents

American Cyanamid Co.

BP 828,797

An aqueous dispersion containing methyl hydrogen polysiloxane, either alone or with another linear or cyclic siloxane, and a cationic amino triazine precondensate, is used to render all kinds of textile materials water-repellent. C.O.C.

**Water-repellent Finish**

Colanese Corp. of America

BP 828,822

A mixture of a silicone and colloidal dispersed silica is used to produce a water-repellent finish on textiles of all types. It is particularly suitable for cellulose triacetate fabrics, to which it also imparts increased abrasion-resistance, tear strength and recovery from creasing. It also decreases the tendency for the fibres to become fused or cut when sewn at high speeds. Presence of the silica reduces the slipping that occurs when cellulose triacetate is silicone-finished in its absence. The treated fabric has a dry, crisp, scroopy handle. C.O.C.

**1-Aziridinyl Phosphine Oxide or Sulphide Polymers for Rendering Hydrophilic Fibres Flame-resistant**

U.S. Secretary of Agriculture

USP 2,901,444

Compounds of formula—



(X =  $-\text{N} \begin{array}{l} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ ; Y = X or dialkylamine; Z = O or S)

polymerise when gently heated in neutral or slightly alkaline aqueous solution. Hydrophilic fibres can be rendered flame-resistant by impregnating them with an aqueous solution of the monomer or partly polymerised monomer and then baking to effect complete polymerisation. Thus cotton cloth was impregnated with 65% of its weight of an aqueous solution at pH 4 containing 25% tris(1-aziridinyl)phosphine oxide, 4% triethanolamine, and 2% cationic softener, dried for 3 min. at 85°C., baked for 5 min. at 140°F. and washed in running hot water for 30 min. The finished cloth had excellent flame resistance and no afterglow, even after boiling for 3 hr. in alkaline soap solution. C.O.C.

**Ketene Dimer Size for Paper**

Hercules Powder Co.

BP 830,099

A ketene dimer is applied, preferably in non-aqueous medium, on to powdered amorphous silica so as to produce a free-flowing powder of particle size  $> 74 \mu$ . The product when added to aqueous pulp slurries gives improved retention and sizing. C.O.C.

Crease-recovery Finish for Cellulosic Fabrics (X p. 383)

Chromium Complexes of Fluorocarboxylic Acids as Oil

Repellent Finishes (X p. 385)

Anti-foam Agents (XI p. 385)

Size imparting High Strength to Paper (XI p. 385)

**IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS****Chemical Constitution and Colour. Mesomeric Degeneration of Coloured Material**

A. van Dornael

*Ind. chim. belge.*, 24 (1959) 463-474*Chem. Abs.*, 54 (25 Feb 1960) 3165

Lecture, 11 references.

C.O.C.

**Intramolecular Hydrogen Bonding and Absorption Spectra in the Ultraviolet. VI—Absorption Spectra of Nitroanilines**

A. E. Lutsikii and V. T. Alekseeva

*Zhur. obshch. khim.*, 29 (Sept 1959) 2992-2998

Absorption spectra (200-480 m $\mu$ ) of nitrobenzene, aniline, and of *o*-, *m*-, and *p*-nitroanilines (NS) in benzene, chloroform, ether, butanol, and 9-8 and 98% H<sub>2</sub>SO<sub>4</sub> are shown. For NS the K band is determined by N $\rightarrow$ V electron transitions, a considerable bathochromic shift and band widening in the case of *o*-nitroaniline being attributed to intramolecular hydrogen bonding. G.J.K.

**"Counter-polarised" Systems and Colour. III—Effects of Substitution of CH<sub>2</sub>NH by CH<sub>2</sub>CH<sub>2</sub>NH and of Methylation of NH in *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>n</sub>-NHC<sub>6</sub>H<sub>4</sub>-p**

V. A. Izmail'skii and V. E. Limanov

*Zhur. obshch. khim.*, 29 (Sept 1959) 2927-2936

Three *N*-methyl derivatives of *N*-*p*-nitrobenzyl- and *N*-*p*-nitrophenethyl-aniline (NA) have been prepared and their reflectance spectra (400-700 m $\mu$ ) measured. Introduction of a second alkyl group (CH<sub>2</sub>NH $\rightarrow$ CH<sub>2</sub>NCH<sub>3</sub>,

and CH<sub>2</sub>CH<sub>2</sub>NH $\rightarrow$ CH<sub>2</sub>CH<sub>2</sub>NCH<sub>3</sub>) or chain lengthening (CH<sub>2</sub>NH $\rightarrow$ CH<sub>2</sub>CH<sub>2</sub>NH and CH<sub>2</sub>NCH<sub>3</sub> $\rightarrow$ CH<sub>2</sub>CH<sub>2</sub>NCH<sub>3</sub>) cause bathochromic shifts which are greater for A = *p*-OCH<sub>3</sub> than for A = H. Hodgson's views (J.S.D.C., 64 (1948) 184) on transmission effects between A and NO<sub>2</sub> groupings in NA are opposed. A method is suggested for constructing reflectance curves for powdered material (or samples of dyed fabric) which would enable their correlation with the corresponding absorption spectra.

G.J.K.

**Kinetics and Mechanism of Diazotisation. XV—Kinetics of the Initial Inorganic Reaction of Diazotisation**

H. Schmid and A. Woppmann

*Mh. Chem.*, 90 (28 Dec 1959) 903-913

The velocity coeff. of the initial reaction during the diazotisation of aniline in perchloric acid and in buffered nitrite soln. at 0°, 15°, and 25°C. respectively, are determined and, on the assumption that this is the primary reaction of formation of nitrosoacidium ion and hydroxonium ion, the data are used for the calc. of the free activation enthalpy  $\Delta G^\ddagger$ , the activation entropy  $\Delta S^\ddagger$ , and the activation enthalpy  $\Delta H^\ddagger$  for the temp. range 0-25°C. Supported by the work of Seel and Schwabell (*Z. anorg. allg. Chem.*, 274 (1953) 169), it follows that only the primary reactions:



and



appear in the kinetic scheme.

H.H.H.

**Reactions of Diazonium Salts with Nucleophiles. V—Substitution of Halogen by Thiocyanate**

E. S. Lewis and H. Suhr

*J. Amer. Chem. Soc.*, 82 (20 Feb 1960) 862-866

Rates of reaction of various *o*- and *p*-substituted halogenobenzenediazonium ions with thiocyanate, which results in substitution of thiocyanate for halogen, have been measured by following the course of the reaction with C<sub>14</sub> labelled thiocyanate ion. Rates were dependent upon the dielectric constant of the solvent used and the order of reactivities in the *p* series was found to be *p*-I > *p*-Br > *p*-Cl > *p*-F. This is explained mainly by the high polarisability of both iodide ion and thiocyanate ion, and also by the solvating effect of the solvent on the smaller halide ions, e.g. fluorine. It is concluded that the reaction is a normal nucleophilic substitution powerfully activated by the diazonium ion group present. F.J.

**Induced Reduction of Methyl Red (C.I. 13020) by Ascorbic Acid**

A. A. Gurevich and N. A. Golosova

*Doklady Akad. Nauk S.S.S.R.*,

126 (11 June 1959) 1125-1128

The mechanism of the reduction of Methyl Red by ascorbic acid in 50% aq. ethanol in presence of H<sub>2</sub>O<sub>2</sub> or oxygen from air (oxidant) and CuSO<sub>4</sub> or FeSO<sub>4</sub> (catalyst) has been investigated. It is found that H<sub>2</sub>O<sub>2</sub>, whether added externally or formed internally (by ultrasonic action on water), reacts initially with ascorbic acid leading to formation of intermediate paramagnetic free radicals (monodehydro ascorbic acid) which, in turn, are capable of reducing Methyl Red. G.J.K.

**Chemistry of Chloranil**

M. R. Venkiteswaran

*Bombay Technologist*, 7 (1957) 39-45*Chem. Abs.*, 54 (25 Feb 1960) 3958

Review of use of tetrachloro-*p*-benzoquinone as a dye intermediate. 19 references. C.O.C.

**Substitution of Halogen in Azo Compounds. VII—Substitution of Chlorine in 2-Hydroxy-8'-chloro-(1,1')-azo Naphthalene by Aryloxy Groups**

B. I. Stepanov and L. N. Arinich

*Zhur. obshch. khim.*, 29 (Sept 1959) 3052-3054

The reaction of an azo dye, 2-hydroxy-8'-chloro-(1,1')-azo naphthalene with ArONa (Ar = C<sub>6</sub>H<sub>5</sub> or *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) in dioxane in presence of cupric acetate leads to substitution of *peri*-chlorine by -OAr. G.J.K.

**Naphthoquinone Dyes**E. Merian *Compt. rend. intern. chim. ind.*, 3P, Liège, 1958(Pub. as *Ind. chim. belge*, Suppl.) 2 (Pub. 1959) 523-531*Chem. Abs.*, 54 (10 Feb 1960) 2747

Review, 64 references.

C.O.C.

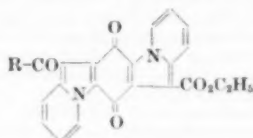


### Quinone Series. XIII—Synthesis of Naphthofurano-pyrrocoline-quinones and Mono- and Dipyrrocoline-quinones

R. V. Acharya, M. S. Mathur, B. Suryanarayana, B. D. Tilak, and M. R. Venkiteswaran

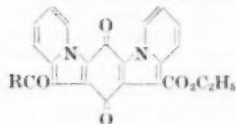
*J. Sci. Ind. Res. (India)*, **17B** (1958) 483-491

Some unsymmetrical substituted benzo-dipyrrocoline-quinones (IA) (IB) have been obtained by interaction of 5-carbomethoxy-7,8-dichlorobenzo-(1,2-b)-pyrrocoline-6,9-quinone (II) and pyridine with acetylacetone. Acetoacetanilide, pyridine and (II) gave (IIIA) and (IIIB)—



(IA) R = CH<sub>3</sub>—

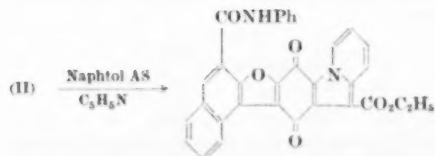
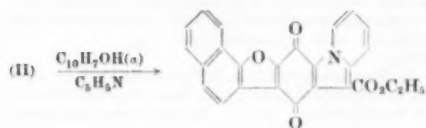
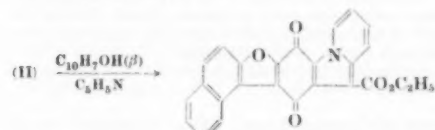
(IIIA) R = C<sub>6</sub>H<sub>5</sub>NH—



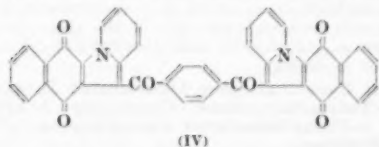
(IB) R = CH<sub>3</sub>—

(IIIB) R = C<sub>6</sub>H<sub>5</sub>NH—

The structures have been confirmed by unambiguous syntheses, conversion to known products and by colour reactions in sulphuric acid. Reaction of (II) with  $\beta$ -naphthol,  $\alpha$ -naphthol, and Naphthol AS (C.I. Azoic Coupling Component 2) gave furano-pyrrocoline-quinones having the following structures—



In order to synthesise substantive vat dyes of the type 2,3-phthaloylpyrrocolines and their aza derivatives, a series of 2,3-phthaloylpyrrocoline-1-carboxy-arylamides has been prepared by interaction of 2,3-dichloro-1,4-naphthoquinone and terephthaloyl-bis-acetylamide. These compounds and derivatives were examined for dyeing properties. (IV) was outstanding as a vat dye.



(IV)

F.J.

### Anthraquinone-acridones

C. F. H. Allen

*Chem. Rev.*, **59** (1959) 983-1030

*Chem. Abs.*, **54** (25 Feb 1960) 3418

Review, 153 references.

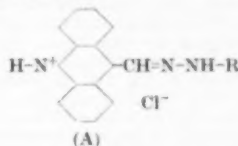
C.O.C.

### Absorption Spectra and Molecular Structure. VI—Colour of the Arylhydrazone-9-acridinium-aldehyde Hydrochlorides Containing Condensed Rings and Heterocyclic Systems

A. A. Kharkharov and G. M. Kharkharova

*Zhur. obshch. khim.*, **29** (Sept 1959) 3042-3048

Seven aryl hydrazone-9-acridinium-aldehyde hydrochlorides (A) of formula—



(A)

(R = phenyl, naphthyl, 5'-benzimidazolyl, acenaphthenyl, anthraquinonyl or 3'-carbazolyl) have been prepared and their absorption spectra (200-800 m $\mu$ ) in 0.2 N-ethanolic HCl measured. It is found that when R = phenyl and naphthyl the bathochromic effect is proportional to the increase in the number of interacting  $\pi$  electrons in the conjugated system irrespective of the presence of an intermittently placed imino group. When R = phenyl, naphthyl, acenaphthyl, and carbazolyl, a further bathochromic effect occurs in proportion to the shift of the electron density from R towards the acridinium nitrogen (H-N<sup>+</sup>). G.J.K.

### Behaviour of Intermediates Produced during Reductive Fading of Eosine in Evacuated Alcoholic Solution

K. Uchida, S. Kato, and M. Koizumi

*Bull. Chem. Soc. Japan*, **33** (Feb 1960) 169-173

The rate of reductive fading of Eosine (C.I. Acid Red 87) in degassed ethyl alcohol solution was measured by irradiation (> 450 m $\mu$ ) over various time intervals at 25°C. The rate constant,  $k$ , was obtained from slope of  $\ln(e^{\text{red}} - 1)$  against  $t$  plot, derived from the equation—

$$\ln(e^{\text{red}} - 1) - \ln(e^{\text{red}} - 1) = 10^3 k I_0 t$$

$c$  = concn. of dye in mol./l.;  $I_0$  = intensity of illumination;  $a$  = average or molar absorption coefficient;  $d$  = solution thickness in cm. Addition of isopentane,  $n$ -hexane, benzene, and cyclooctatetraene generally retarded the reaction while hydrocarbons containing a double bond, i.e. cyclohexene and  $n$ -hexene, promoted the fading rate. Retarding effect was probably due to deactivation of the triplet state,  $D$ , of the dye by the added substance. A modified mechanism is given in which the promoting effect is due to formation of a molecular complex between  $D$  and ethyl alcohol before formation of the semiquinone radical of eosine. F.J.

### Primary Processes in the Fading of Eosine by Flash Technique

S. Kato, T. Watanabe, S. Nagaki, and M. Koizumi

*Bull. Chem. Soc. Japan*, **33** (Feb 1960) 262-265

Techniques of flash photolysis and flash spectroscopy have been used to study reductive fading of Eosin (C.I. Acid Red 87) and Uranine (C.I. Acid Yellow 73) in degassed ethanol solution. At a flash time interval of 0.6 millisecon. the absorption spectra of transient species could be obtained. For Eosin, three absorption maxima at 373, 410 and 450 m $\mu$  were observed, the peak at 410 m $\mu$  being absent at a flash interval of 5 millisecon. Similar results obtained for Uranine in alcohol except that the 410 m $\mu$  peak was not found. Transient spectrum of the semiquinone with a lifetime order of milliseconds was established. In the case of Eosine the 410 m $\mu$  peak was attributed to complex formation between dye and solvent. A scheme for primary processes of reductive fading including this complex formation is given. F.J.

### Constitution and Dyeing Properties of Dihydroxy-formazan Dyes

H. Ziegler

*Compt. rend. congr. intern. chim. ind.*, **3P**, Liège (1958)

(Pub. as *Ind. chim. belge, Suppl.*) **2** (Pub. 1959) 532-7

*Chem. Abs.*, **54** (25 Feb 1960) 3959

Describes the properties of a series of Cu complexes of NN'-bis(o-hydroxyphenyl)-C-phenylformazans. These dyes are prepared by coupling two amines either with phenylformylacetic acid or its esters. They dye protein fibres from neutral or slightly acid baths. C.O.C.



**Constitution and Colour of Dioxazine Dyes**

R. L. Lantz

*Compt. rend. congr. intern. chim. ind.*, 31<sup>e</sup>, Liège (1958)  
(Pub. as *Ind. chim. belge*, Suppl.) 2 (Pub. 1959) 521-2  
*Chem. Abs.*, 54 (25 Feb 1960) 3958

Describes synthesis of dioxazine dyes, very similar to the commercial sulphonated triphenyldioxazine dyes, but differing in having naphthalene instead of benzene rings linked to both ends of the dioxazine skeleton. These dyes are red and their sulphonated derivatives are also red while their analogues are blue dyes. This difference is ascribed to the greater oxidisability of the terminal naphthalene groups giving the diquinonic derivatives better stability than the monoquinonic derivative. The red diquinonic dye can be converted into the blue monoquinonic derivative by a stepwise reduction, the reverse reaction occurring in air. Introduction of  $\text{CH}_3$  groups into the central ring of dioxazine which should promote formation of the monoquinonic derivative has too small effect to stabilise the latter. C.O.C.

**Crystal Violet (C.I. 42555). Determination of the Rate of Protolysis in Aqueous Solution**

R. Cigén

*Acta Chem. Scand.*, 12 (1958) 1456-1475 (in German)  
*Chem. Abs.*, 54 (24 Feb 1960) 2907

The protolysis of Crystal Violet, which occurs in a number of coloured forms in equilibrium with one another and also in a number of hydrated forms, occurs instantaneously, whereas hydration requires a measurable time. Absorption curves are given for 3 coloured forms and 5 dissociation constants, 4 hydration constants and 8 velocity constants are also given. The measurements were made spectrophotometrically at 20°C. and constant ionic strength of 0.5 M. C.O.C.

**CDC 13(1029) Dye, Ink Blue, for Ink Industry****CDC 13(1030) Dye, Methylene Blue, for Ink Industry**

Two new Indian draft standards now available from either the Indian authorities or the British Standards Institution. C.O.C.

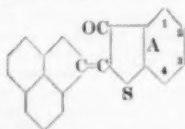
**Radiation-induced Synthesis of Lauth's Violet (C.I. 52000)**

P. Balcastic and M. Magat

*J. Phys. Chem.*, 63 (1959) 976-8  
Spectroscopic and chemical evidence indicates that  $\gamma$ -ray irradiation of aerated solutions of *p*-phenylenediamine and  $\text{H}_2\text{S}$  at pH > 1 leads to formation of C.I. 52000. Isolation and purification of the dye are described and some kinetic results given. C.O.C.

**Derivatives of Benz(c,d)-indoline. IV—Products of the Condensation of 1-Methyl-2-Methylbenz-(c,d)-indolinium Methylsulphate with 3-Oxythionaphthenes**

N. S. Dokunikhin, G. M. Oksegendler, and Ya. B. Shteinberg *Zhur. obshch. khim.*, 29 (Oct 1959) 3361-3363  
Six new dyes of formula—



which will dye cellulose acetate and 6-nylon fibres red and mauve have been prepared by condensing 1-methyl-2-methylbenz-(c,d)-indolinium methylsulphate with substituted 3-oxythionaphthenes. Absorption max. of the dyes in *m*-xylene for different substituents in A

(3- $\text{OC}_2\text{H}_5$ ; 3-Cl; 1- $\text{CH}_3$ , 3-Cl; 1,2- $\text{CH}=\text{CH}_2$ ); and 3,4- $\text{CH}=\text{CH}_2$ ) are given. G.J.K.

**Formation of Tetraazaporphin from Phthalic Anhydride and its Reduction Products**

M. Shigemitsu

*Bull. Chem. Soc. Japan*, 32 (June 1959) 541-543  
Attempts were made to prepare tetraazaporphins from phthalic anhydride (I), 3,4,5,6-tetrahydrophthalic anhydride (II), 1,2,3,6-tetrahydro-*cis*-phthalic anhydride (III), hexahydro-*cis*-phthalic anhydride (IV), and 3,6-endomethylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride

(V). Copper phthalocyanine (VI) was obtained from (I) in good (90-5%) yield and cyclohexenotetraazaporphin (VII) in poor (4-1%) yield from (II). (III), (IV), and (V) did not give tetraazaporphins. Reflectance curves and infrared spectra are given and it is concluded that when aromaticity is weak or very small tetraazaporphins cannot be produced. When the double bond between carbonyl groups is not reduced, tetraazaporphin is obtained in small yield. F.J.

**X-Ray Diffraction Studies on Copper Phthalocyanine (C.I. 74160) and its Chlorinated Derivatives**

M. Shigemitsu

*Bull. Chem. Soc. Japan*, 32 (June 1959) 607-616

Electron photomicrographs, X-ray diffraction patterns and reflectance curves were obtained with copper phthalocyanine, copper tetra-3-chlorophthalocyanine, copper tetra-4-chlorophthalocyanine, copper octa-3,6- and -4,5-chlorophthalocyanine (C.I. 74255) and copper hexadecachlorophthalocyanine (C.I. 74260) both in needlelike ( $\alpha$ ) and granular ( $\beta$ ) forms. The  $\alpha$  form was obtained by sublimation, or in the case of chlorinated derivatives by condensation of the various chlorophthalic anhydrides with urea and copper in trichlorobenzene. The  $\beta$  form was obtained by dissolving in chlorosulphonic acid and pouring into ice water. Crystal growth was inhibited by increase in chlorination.  $\beta$  form derivatives containing > 8 Cl atoms tended to revert to the more stable  $\alpha$  form like copper phthalocyanine, when heated in high b.p. solvents. F.J.

**Reduction of Copper Hexadecachlorophthalocyanine (C.I. 74260)**

M. Shigemitsu

*Bull. Chem. Soc. Japan*, 32 (June 1959) 544-547

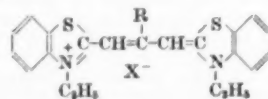
Copper hexadecachlorophthalocyanine was reduced and the product reprecipitated from solution in chlorosulphonic acid by pouring into water. The reduced product was also reoxidised and a second sample heated at 250-255°C. for 3 hr. in nitrogen. Examination of the products from each stage, using chemical analysis, X-ray diffraction, reflectance curves, and infrared spectra, suggested that chlorination of copper phthalocyanine (C.I. 74160) seemed to facilitate hydrogenation at C=C and C=N bonds and that darkening of colour occurs as in reduced vat dyes. F.J.

**Chemistry of Cyanine Dyes. XIV—Condensation of Aromatic and Heterocyclic Ketones with Quaternary Salts of 2-Methylbenzthiazole and Transformation of the Products into Cyanine Dyes**

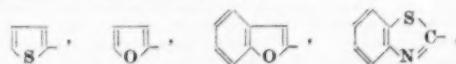
I. K. Ushenko

*Zhur. obshch. khim.*, 29 (Oct 1959) 3364-3376

Reaction of a series of quaternary salts of  $\beta$ -substituted 2-propenyl-benzthiazole with 2-methylmercaptobenzthiazole ethyl iodide yielded 24 different dyes, mainly of formula—



and also a few benzo- and dibenzo-thiacarbocyanines ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{-}p, \text{C}_6\text{H}_4\text{OCH}_3\text{-}p, \text{C}_6\text{H}_4\text{OCH}_3\text{-}o, \text{C}_6\text{H}_4\text{NHCOCH}_3\text{-}p, \text{C}_6\text{H}_4\text{NH}_2\text{-}p, \text{C}_6\text{H}_4\text{OH-}p, \text{C}_6\text{H}_4\text{OH-}o, \text{C}_6\text{H}_5\text{-}a, \text{C}_6\text{H}_4\text{NO}_2\text{-}p$ ).



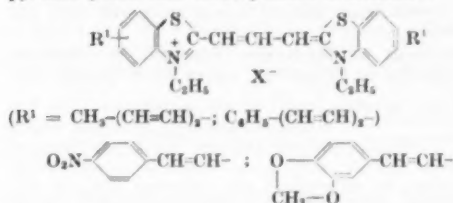
$\text{X} = \text{I}$ , or  $\text{Br}$ .  $\text{R} = \text{Alk}$  causes a hypsochromic,  $\text{R} = \text{Ar}$  a weak bathochromic, whilst  $\text{R} = \text{heterocyclic group}$  a considerable bathochromic shift of the absorption max. Preparation, and physical and chemical data of the dyes are given in detail. G.J.K.

**Cyanine Dyes containing Unsaturated Substituents III—Thiacarbocyanines Containing  $\beta$ -Arylvinyl and  $\gamma$ -Phenylbutadienyl Groupings in 5,5'- and 6,6'-Positions**

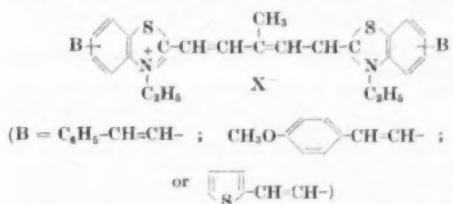
M. A. Al'perovich, I. K. Ushenko, and L. N. Tyurina  
*Zhur. obshch. khim.*, 29 (Oct 1959) 3376-3383

Reaction of *p*-nitrocinnaic, piperonylacrylic, cinnamic, styrylacrylic, and ascorbic acid with 2-methyl-5-, 2-methyl-6-, and 2-ethyl-6-benzthiazolyl diazonium hydrochloride

yields new benzthiazole derivatives (BTD) containing unsaturated groupings in 5- and 6-positions of the benzthiazole nucleus. Condensation of quaternary salts of BTD (QBTD) with *ortho* esters of carboxylic acids in pyridine yields nine carbocyanines of formula—



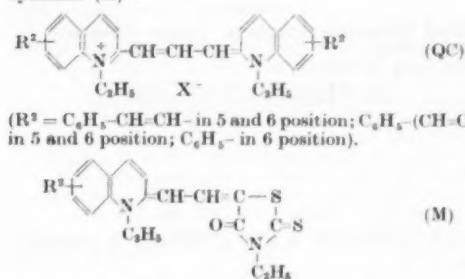
Condensation of QBTD with dianil of methylmalonic aldehyde yields thiadcarbocyanines of formula—



Introduction of R<sup>1</sup> and B causes a considerable bathochromic effect.

#### IV—Quinocyanines with Phenylbutadienyl and Styryl Groupings in the Quinoline Nucleus

M. A. Al'perovich and I. K. Ushenko *Ibid.*, 3384–3391 Using Meerwein's reaction, styryl- and *o*-phenylbutadienyl derivatives of quinaldine have been synthesised and the corresponding quaternary salts prepared. Condensation of the latter with orthoformic ester (in pyridine), and 3-ethyl-5-(acetanilidomethylene)-rhodamine (in ethanol), yields quinocarbocyanines (QC) and merocyanines (M)—



(R<sup>1</sup> = H; C<sub>6</sub>H<sub>5</sub>-(CH=CH)<sub>2</sub> in 5 and 6 position; C<sub>6</sub>H<sub>5</sub>-CH=CH- in 5 and 6 position). Introduction of unsaturated substituents into the quinoline nucleus of QC or M causes a strong bathochromic effect. Physical chemical, and preparative data of these dyes are tabulated.

G.J.K.

#### Synthetic Dyes

##### XIII—Asymmetric Monomethinquinocyanines

G. T. Pilyugin and E. P. Opanasenko

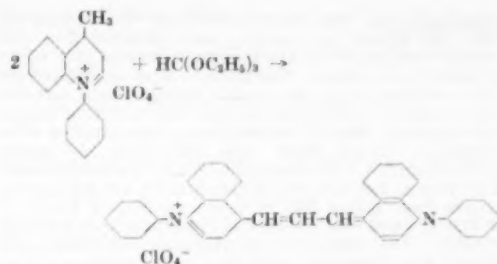
*Zhur. obshch. khim.*, 29 (Sept 1959) 3065–3076

21 asymmetric monomethinquinocyanines have been prepared and their absorption spectra (440–640 mμ.) in ethanol, m.p., and microanalytical data tabulated. Substitution of alkyl by aryl on the nitrogen of the benzthiazole ring causes a weak bathochromic shift. The absorption max. in both isomeric iso- and quinothia-pseudocyanines are affected by the position of the phenylene grouping in the molecule.

##### XIV—Synthesis of N-Phenyllepidinium Perchlorate and Some of its Transformations

G. T. Pilyugin and B. M. Gutsulyak *Ibid.*, 3076–3079

N-phenyllepidinium perchlorate, obtained from diphenylamine by Beier's reaction, undergoes condensation to a symmetrical cyanine dye—



an alcoholic solution of which has absorption max. of 718 mμ., compared with 710 mμ., for the ethyl analogue.

G.J.K.

#### Mechanism and Kinetics of Oxidative Colour Coupling

J. Eggers

*Phot. Korrr.*, 95 (1959) 115–124, 131–4

*Chem. Abs.*, 54 (16 Feb 1960) 2056

Review of work on the oxidation of *p*-amino-N,N-diethylaniline, coupling with 2- and 4-equivalent couplers, deamination and side-reactions, and formation of dye from leuco compounds. Several partial reactions important during coupling are suggested and rates or equilibrium constants for the above developer are given. 32 references. C.O.C.

#### Fastness to Light of Sensitising Dyes

R. A. Jeffreys

*Compt. rend. congr. intern. chim. ind.*, 3<sup>re</sup>, Liège (1958)

(Pub. as *Ind. chim. belge*, Suppl.), 2 (Pub. 1959) 495–8

*Chem. Abs.*, 54 (25 Feb 1960) 3959

Fastness to light of a series of N,N'-diethyltrimethincyanine iodides in methyl alcohol is given as "fading value", i.e. the time required to reduce the absorption by half at the maximum adjusted for the output of the light at that wavelength. Increase in fastness is correlated with decrease in basicity of the heterocyclic nucleus. For dyes having the same heterocyclic nucleus the fading values decrease with increase in length of the polymethine chain. A series of methinocyanines derived from 3-alkyl-rhodanines showed the same correlation between fading values and basicity. A mechanism is proposed for the decomposition of the dye. C.O.C.

#### Anthocyanins. XXXI—Commelin, a Crystalline Blue Metallo-anthocyanine from *Commelina* flowers

S. Mitsui, K. Hayashi, and S. Hattori

*Proc. Japan. Acad.*, 35 (1959) 169–174 (in English)

*Chem. Abs.*, 54 (10 Feb 1960) 2501

Evidence showing that commelin consists of 4 mol. of swobanin (delphinidin-3,5-diglucoside (C.I. 75190) + *p*-coumaric acid) held together with 1 atom of Mg and weakly linked to an unknown yellowish substance. C.O.C.

#### Fluorescent Pigments in the Skins of Ornamental Fishes

T. Kauffmann

*Z. Naturforsch.*, 14b (1959) 358–363

*Chem. Abs.*, 54 (10 Feb 1960) 2618

The following have been isolated: the blue fluorescing ichtyopterin or 6-(1,2-dihydroxypropyl)isoxanthopterin, the bluish violet fluorescing isoxanthopterin and the bright blue fluorescing 2-amino-4-hydroxypteridine carboxylic acid. A number of pigments of unknown constitution or believed to be identical with other known natural pigments were also isolated. C.O.C.

#### Solvent Dyes

W. Carr

*Compt. rend. congr. intern. chim. ind.*, 3<sup>re</sup>, Liège, (1958)

(Pub. as *Ind. chim. belge*, Suppl.), 2 (Pub. 1959) 395–8

(in English)

*Chem. Abs.*, 54 (25 Feb 1960) 295–8

The poor keeping properties of some solutions of solvent dyes and the discrepancies in solubility data obtained by different workers are explained by assuming that the solutions were partly true solutions and partly dispersions. Experimental evidence supporting this assumption is given. Experimental confirmation was obtained that the apparent solubility and the keeping properties of solutions were increased by suitable additives acting as dispersing agents, although the effects of the agents were specific to certain dyes. Solutions of dyes in methylated spirits,

apparently free from suspended matter, were stirred for 1 hr. and filtered (no residues were obtained from the weaker solutions while the stronger solutions gave slight to heavy precipitates). The filtrates were centrifuged for 1 hr. at 3,000 r.p.m. (no further precipitation), and the concentrations determined to give the following results (dye apparent original concentration, concentration after filtration): Grasoil Fast Blue 3B (acid dye-amine derivative); 2, 4, 6, 8, 10 and 12 to 2, 4, 6, 6, 6 and 6; Grasoil Fast Blue A; 2, 4, 6, 8, 10 and 12 to 2, 4, 4-5, 4-5, 4-2 and 4-4; Grasoil Fast Yellow 3GL (C.I. Solvent Yellow 27); 1, 2, 3, 4, 5, 6, 7 and 8 to 1, 1-42, 1-42, 1-41, 1-42, 1-43, 1-42 and 1-42%. The effects of incorporating additives with Grasoil Fast Blue 3B in alcohol were (additive, % in mixture, apparent % solubility of mixture, maximum storage period (in days before setting): none, 4, 1; di-*o*-tolylguanidine (I) 20, 7, 3; I, 33, 7, 4; urea 20, 8, 1; urea 33, 8, 7; 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub> (II) 20, 8, 2; II 33, 9, 3; II 43, 10, 7-14. Shellac tritoyl phosphate and dibutyl phthalate also showed definite stabilising action in alcohol. In ketonic systems all products which gave improvements in alcohol were ineffective, but triethanolamine oleate (III) and a non-ionic fatty alcohol-ethylene oxide condensate (IV) gave very marked improvement, III giving the better results. The improvement was particularly marked with metal-complex dyes. Metal-complex dyes, normally insoluble in xylene, dissolved or appeared to dissolve to 0.5-1.0% when III or IV was added, IV being the more effective. C.O.C.

#### Toxicity of Some Synthetic Organic Dyes

J. F. Reith *Chem. Weekblad.*, **55c** (1959) 623-631  
*Chem. Abs.*, **54** (25 Feb 1960) 3957

Review, 43 references.

#### Dyes for Preserving Wood

J. W. Weaver, E. B. Jeroski, and I. S. Goldstein  
*Forest Prods. J.*, **9** (1959) 372-4  
*Chem. Abs.*, **54** (25 Feb 1960) 3827

Southern yellow pine cubes were treated by the full-cell process with 2% aqueous solutions of various dyes, leached for several days in running water, dried and given soil-block tests with *Leptinus lepidus*, *Poria monticola*, and *Lenzites trabea*. The most effective fungistatic dye was Ethyl Violet (C.I. 42600). Malachite Green (C.I. 42000), Setoglucine (C.I. 42025), and Brilliant Green (C.I. 42040) were much less effective. C.O.C.

#### Dispersion of Pigments by Ultrasonics

M. Górski *Przemysł Chemiczny*, (1) (1959) 48-51  
*Polish Technical Abstracts*, No. 3 (35) (1959) 79

In investigations on the preparation of viscous dispersions suitable for the mass coloration of viscose the influence of ultrasonics on the particle size of suspensions of Pigment Green B (C.I. Pigment Green 8), Phthalocyanine Blue B (C.I. Pigment Blue 15) and Carbon Black (C.I. Pigment Black 6 and 7) was studied. In these studies the following factors were varied: intensity and time of ultrasonic irradiation, the medium in which the pigments were dispersed, concentration and volume of the sample, and the thickness of the bottom of the vessel in which irradiation was carried out. Suitable dispersions of Pigment Green B and Phthalocyanine Blue B were obtained on a laboratory scale. C.O.C.

#### Yellow Pigments

E. Herrmann *Farbe u. Lack*, **65** (1959) 636-646  
*Chem. Abs.*, **54** (25 Feb 1960) 3989

An account of the manufacture, chemical composition, properties and uses of Yellow Iron Oxide (C.I. Pigment Yellow 42 and 43), Zn and Pb chromates (C.I. Pigment Yellow 36 and 34), Cadmium, Naples and Titanium-Nickel Yellows (C.I. Pigment Yellow 37, 41, and 53) and various organic yellow pigments. C.O.C.

#### Influence of the Cations and Anions of Directing Substances on the Colour and Properties of Yellow Iron Oxides (C.I. 77492)

M. Krantz and A. Witkowska  
*Przemysł Chemiczny*, (2) (1959) 88-91  
*Polish Technical Abstracts*, No. 3 (35) (1959) 85

Study of the influence of anions connected with the Cd<sup>2+</sup> cation which is highly active in this respect and of ions of Na and K which are inactive. This method allows elimination of the action of cations and enables study of the behaviour of sulphate, acetate, chloride, bromide, and iodide anions alone. In addition to the action of cations

on the trace substance, its cations also exert a selective influence on the properties of the yellow iron oxides. This directing effect is caused by the joint action of the cation with an appropriate anion. Generally the directing action of anions alone is less energetic and sometimes less advantageous than that of anions connected with the Cd<sup>2+</sup> cation. C.O.C.

#### Replacement of Hydrogen Peroxide by Sodium Hypochlorite in Preparing Yellow Iron Oxides (C.I. 77492)

A. Krause, M. Kranz, and J. Fijatkowska  
*Przemysł Chemiczny*, (5) (1959) 290-2  
*Polish Technical Abstracts*, No. 4 (36) (1959) 91

Aqueous NaOCl (20% active chlorine) is completely satisfactory as an oxidant for replacing H<sub>2</sub>O<sub>2</sub> in the manufacture of yellow iron oxides, the products being equally as good both as regards colour and physical structure. The NaOCl should be added slowly and somewhat larger amounts of "directing substances" (CdBr<sub>2</sub>, CdI<sub>2</sub>, CdSO<sub>4</sub>, KBr, and KI) (0.05 g./3 g. Fe) are needed. C.O.C.

#### A Yellow, Crystalline Tin (II) Hydroxide Stabilised by Silicic Acid

H. Weber *Z. anorg. u. allgem. Chem.*, **301** (1959) 109-112  
*Chem. Abs.*, **54** (25 Feb 1960) 3026

Amorphous gels prepared by mixing solutions of SnCl<sub>2</sub>, Na<sub>2</sub>SiO<sub>3</sub>, and NaOH are converted on standing for days at room temperature, more rapidly on boiling or heating in autoclaves, to bright yellow crystalline products stable to < 300°C. in air and unaffected by several hours exposure to ultraviolet radiation. The specific surface and colour depend on the pH (2-10) at precipitation, the SiO<sub>2</sub>:Sn(OH)<sub>2</sub> ratio (0.2-1), and the crystallisation temperature and time. C.O.C.

#### Standard X-ray Diffraction Powder Patterns

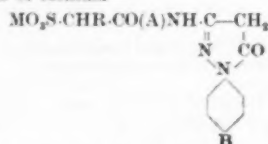
H. E. Swanson, M. I. Cook, T. Isaacs, and E. H. Evans  
*U.S. National Bureau of Standards Circular* 539,  
**9** (25 Feb 1960) pp. 64

Gives the X-ray diffraction powder patterns of 43 inorganic compounds including several of use as pigments. There is also a cumulative index to the whole of the 9 volumes. C.O.C.

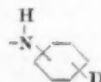
#### PATENTS

#### Acylyated 3-Aminopyrazolone Colour Couplers

General Aniline **USP 2,902,366**  
Compounds of formula—



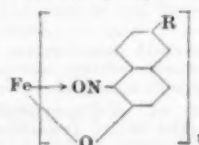
(R = Alk of 8-18 C; B = H or a carbamyl or sulphonyl group; A =



(D = CO, COCH<sub>3</sub> or COCH<sub>2</sub>O); M = H, NH<sub>4</sub> or alkali metal), e.g. 1-phenyl-3-(3'-*o*-sulphosteamido)-benz-amido-5-pyrazolone, are non-diffusing magenta colour couplers of adequate stability to light and heat. C.O.C.

#### Iron Complexes of $\alpha$ -Nitroso- $\beta$ -naphthols—Green Dyes for Wool and Nylon

General Aniline **BP 829,917**  
Fe complexes of  $\alpha$ -nitroso  $\beta$ -naphthol dyes of formula—

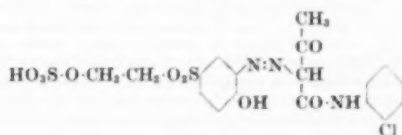


(R = SO<sub>2</sub>CH<sub>3</sub>, SO<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> or morpholino-sulphonyl) are green dyes for wool and nylon, characterised by good neutral dyeing affinity, bright shade, and

excellent wash fastness. They are obtained by condensing a 2-naphthol-6-sulphonic acid with benzene sulphonyl chloride to give the corresponding benzene sulphonyl ester, which is then treated with  $\text{PCl}_5$  to give the benzene sulphonyl ester of 2-naphthol-6-sulphonyl chloride (I). This is condensed with the requisite amine to introduce group R and the resulting sulphonamide subjected to hydrolysis, nitrosation, and iron complex formation with  $\text{FeCl}_3$  in absence of sodium potassium tartrate. For  $\text{R} = \text{SO}_3\text{CH}_3$ , I is reduced with  $\text{Na}_2\text{SO}_3$  to the sulphonic acid and this methylated with  $\text{CH}_3\text{I}$ . Previously recorded dyes of similar constitution but with different substituents R, e.g.  $\text{SO}_3\text{Na}$ ,  $\text{SO}_3\text{NH}_2$ , had poor wash fastness and dull dyeings. A.T.P.

#### Metal(Cobalt)-complex Monoazo Dyes Containing Vinylsulphone Groups—Reactive Dyes for Wool, etc.

BP 831,128  
The metal complexes from 2 mol. of suitable *oo'*-dihydroxymonoazo compounds containing 1 or 2  $\text{SO}_3\text{CH}_2\text{CH}_3$  groups, combined with 1 atom of Co, dye wool and polyamide fibres from neutral or weakly acid baths, the vinylsulphone group combining chemically with the fibre. Instead of vinylsulphone groups, the group  $\text{SO}_3\text{CH}_2\text{CH}_2\text{O}-\text{SO}_3\text{H}$  may be present since it is readily converted to vinylsulphone by alkalis. Thus 2-amino-phenol-4- $\beta$ -hydroxyethylsulphone is sulphated at the side-chain O atom, and the product is diazotised and coupled with acetoacet-*o*-chloroanilide giving—

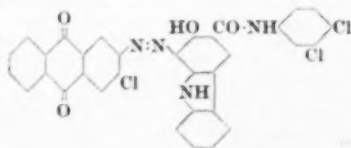


Stirring at 80–85°C. with aq.  $\text{CoSO}_4$  gives the metal-complex which dyes wool reddish yellow of good fastness to wet treatments and light. E.S.

#### Anthraquinoneazo Pigments

General Aniline USP 2,900,380

The leuco sulphuric acid esters of aminohalogeno-anthraquinones are diazotised and coupled with arylides of hydroxycarbazolecarboxylic acids, and the leuco compounds are then oxidised to give the title compounds. Thus the Na salt of 2-amino-3-chloroanthraquinone-9,10-dihydrodisulphuric acid ester is diazotised with aq.  $\text{HCl}$  and  $\text{NaNO}_2$  at 0–5°C. and coupled with an alkaline soln. of 2-hydroxycarbazole-3-carboxy-3',4'-dichloroanilide. The soluble monoazo compound so formed is heated with aq.  $\text{NaNO}_2$  and aq.  $\text{HCl}$  then added to hydrolyse and oxidise the leuco-sulphuric ester groups, giving the brown insoluble pigment—



E.S.

#### Water-soluble Azophthalocyanine Direct Dyes

FBY BP 830,920

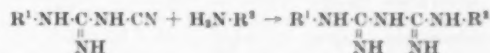
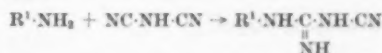
Phthalocyanine-sulphonamide and -carbonamide derivatives  $\text{Pe}(\text{X}-\text{R})_n$  ( $\text{Pe}$  = radical of a phthalocyanine;  $\text{X} = \text{SO}_3$  or  $\text{CO}$ ;  $\text{R}$  = amino group containing radical of naphthalene, pyrazolone, or acylacetarlamide series linked to X via its amino group and containing also a coupling position;  $n = 1-4$ ) are coupled with diazo compounds of arylamines containing at least one water-solubilising substituent, to give the title dyes. The bright greens obtained when R is a pyrazolone or acylacetarlamide radical are particularly valuable. Thus 1-*p*-aminophenyl-3-methyl-5-pyrazolone is condensed with Cu phthalocyanine-(3')-trisulphonchloride, and the product is coupled with diazotised orthanilic acid to give a bright green. E.S.

#### Biguanide Polyazo Dyes

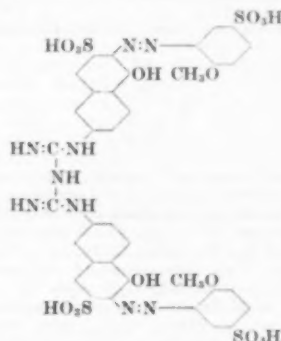
American Cyanamid Co.

USP 2,898,332

Primary arylamines react in two stages with dicyanamide thus—



By using e.g. J acid as the arylamine, the products may be coupled with diazo compounds to give direct dyes, which may be metallised if the components chosen give rise to a chelating system such as *oo'*-dihydroxyazo. Thus 2 mol. of J acid are condensed with 1 mol. of sodium dicyanamide by boiling with water for 22 hr. The product is coupled with 2 mol. of diazotised 2-aminoanisole-4-sulphonic acid, giving—

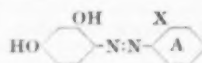


Boiling with ammoniacal  $\text{CuSO}_4$  gives the Cu-complex which is a reddish-purple direct dye. E.S.

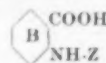
#### Metal-complex Azoic Browns Developed by Neutral Steaming

Fran Monazo compounds—

BP 830,970



(X = OH or COOH; the ring A may contain Hal, Alk, OAlk,  $\text{NO}_2$ , sulphonamide, acylamino, or sulphone groups) are complexed with salts of metals of atomic no. 24–29 in presence of amines or organic amides, and mixed with triazenes obtained by condensing diazo and tetrazo compounds of arylamines, free of solubilising substituents, with anthranilic acid derivatives—



(the ring B may carry Hal substituents; Z = carboxyalkyl or hydroxyalkyl). When thickened, printed on cotton, and steamed under neutral conditions, brown azoic prints are produced. Thus 2,2',4'-trihydroxyazobenzene dissolved in aq.  $\text{NaOH}$  is stirred with  $\text{CoSO}_4$  and monoethanolamine for 1 hr. in the cold, and aq.  $\text{HCl}$  is then added to precipitate the complex, which is mixed with the triazene obtained by condensing diazotised 2-amino-4-chloroanisole with N-(2-carboxyphenyl)glycine. E.S.

#### Reactive Dyes for Cellulose, having a $\gamma$ -Halogeno- $\beta$ -Hydroxypropylsulphamyl Group

ICI BP 830,847

Dyes of the azo, anthraquinone, and especially the phthalocyanine series containing at least one  $\text{SO}_3\text{H}$  or  $\text{COOH}$  group and at least one sulphamyl group in which the N atom carries at least one group  $\text{CH}_2\text{-CH}(\text{OH})\text{-CH}_2\text{-Hal}$ , react with cellulose under alkaline conditions. Thus copper phthalocyanine is heated in chlorosulphonic acid to give substantially the tetra-(3')-sulphonchloride, which is suspended in water at < 5°C. and condensed with 3-chloro-2-hydroxypropylamine in presence of  $\text{NaHCO}_3$ . The water-soluble product



is substantially the di(sulphon- $\gamma$ -chloro- $\beta$ -hydroxy-propylamide)-disulphonic acid of copper phthalocyanine, and gives greenish-blues on cellulose when applied as a reactive dye in conjunction with alkali. E.S.

### Anthraquinone Vat Dyes

FBy

USP 2,901,479

Olive green vat dyes of excellent fastness to washing are obtained by treating the sulphonic acid chlorides of the condensation products of either (i) Bz-1-benzanthronyl-amino-dianthrims with an  $\text{AlCl}_3$  complex compound, or (ii) Bz-1-benzanthronyl-amino-dianthrims with alcoholic KOH, with primary or secondary organic bases. Generally, the dyes described in USP 2,805,224 are chlorosulphonated and the resulting sulphonyl chloride converted to the sulphonamide with, e.g.,  $\text{NH}_3$ ,  $\text{NH}(\text{CH}_3)_2$ , piperidine, etc. A.T.P.

### Anthraquinone-1,2,4-triazoles

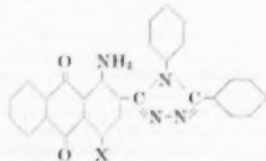
American Cyanamid Co.

USP 2,898,343

Vat dyes or vat dye intermediates of formula—



( $\text{R}^1$  = a 2-anthraquinonyl radical which may be substituted in up to two of the 1, 4 or 5 positions, by H,  $\text{NO}_2$ , Cl,  $\text{NH}_2$ , benzamido, thienonylamino or *m*-trifluoromethyl-benzamido;  $\text{R}^2$  = Ar, which may be substituted by up to two of H,  $\text{CH}_3$ ,  $\text{OCH}_3$ , Cl, Br,  $\text{CF}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_2$ , OH or  $\text{NH}(\text{C}_2\text{H}_5)_2$ ). They are obtained by condensing a carbonylhydrazide,  $\text{RCONHNH}_2$ , with a chlorimide  $\text{R}^2\text{NCClR}^3$ . Ring closure is sometimes spontaneous but cyclising agents, e.g.  $\text{POCl}_3$ ,  $\text{H}_2\text{SO}_4$ , may be used. The anthraquinone residue can be in either of the two reactants. This method is used where the anthraquinone residue carries no substituents or has a Cl group in the 1-position; but is unsatisfactory where a substituent is also present in the 4-position. Here, an anthraquinone-2-carboxylic acid is converted to an arylamide and thence with, e.g.  $\text{PCl}_5$ , to the anthraquinonyl aryl chlorimide. The latter yields an anthraquinonyl-2-carboxylic arylidene hydrazine with hydrazine or its hydrate and thence the 1,2,4-triazole with a diaryl chlorimide. Similarly, 1-aminoanthraquinone-2-carboxylic anilide (20) is heated to solution at  $100^\circ\text{C}$ . with  $\text{PCl}_5$  (11.6) in chlorobenzene (400). Hot filtration and cooling of the filtrate gives 1-aminoanthraquinone-2-carboxylic acid phenylimide chloride; which (12) is then heated to  $80-90^\circ\text{C}$ . in dry freshly distilled dioxane (250) and hydrazine hydrate (10) added dropwise. The mixture is stirred hot until reaction is complete and 1-amino anthraquinone-2-carboxylic acid anilide hydrazine collected and washed with methanol. This (6) is finally refluxed in *o*-dichlorobenzene (160) and pyridine (10) with *N*-phenyl benzimidyl chloride (3.2) to give the red vat dye ( $\text{X} = \text{H}$ ).



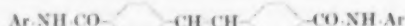
If  $\text{X} =$  benzamido, the dye is blue. A.T.P.

### Acylamino Anthraquinone-Stilbene Vat Dyes

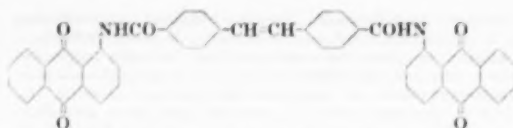
American Cyanamid Co.

USP 2,903,450

Acylamino anthraquinone vat dyes having good substantivity and fastness are of formula—



(Ar = a vatable organic radical, especially anthraquinone, dianthrims, anthraquinone-acridone, dibenzanthrone, anthrapyrimidine or pyrazoleanthrone). Thus the very bright golden yellow vat dye—



is obtained by heating 4,4'-stilbene-dicarbonyl chloride (2.7) and 1-aminoanthraquinone (4) in nitrobenzene (72) to  $140^\circ\text{C}$ . and keeping the mixture at  $140-150^\circ\text{C}$ . until reaction is complete. The product is isolated by cooling, filtering, and washing the cake with nitrobenzene and methanol. Substantivity is generally very high, especially for acylaminoanthraquinone vat dyes. A.T.P.

### Oxidation of Leuco Vat Dyes during Manufacture

American Cyanamid Co.

USP 2,898,337

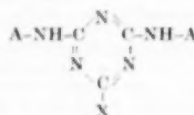
Long and expensive air oxidation of leuco vat dyes of e.g. the indanthrone, isodibenzanthrone, pyranthrone, and 5,5'-dichloro-7,7'-dimethyl thioindigo classes is avoided by an oxidation process involving, basically, reduction of the pH of a slurry of leuco vat dye to below 10, preferably 6.5-10, in absence of reducing agents. This can be effected by filtration of the leuco vat cake from a slurry in a medium of insufficient volume and temperature to dissolve it and then either (i) washing the cake with a solution of lower pH until pH of the cake is reduced to below 10, followed by water washing, or (ii) reslurrying the cake and reducing the pH of the slurry to below 10, filtering and washing with water. pH lowering can be brought about by any water soluble solution of pH below 10, e.g. HCl, HOAc,  $\text{H}_2\text{SO}_4$ , borax boric acid mixtures, and, preferably,  $\text{NaHCO}_3$  or  $\text{KHCO}_3$ . Small amounts of oxidising agents, e.g.  $\text{H}_2\text{O}_2$ , may be added in difficult cases. Thus, excess Na hydrosulphite is added to an alkaline slurry of crude indanthrone which is partly in the leuco state and partly oxidised; this reduces the dye completely to the leuco form. The crystallised leuco compound is filtered and the cake washed with 1% aq.  $\text{NaHCO}_3$  until the filtrates have pH below 10. Water washing to neutral results in an excellent yield of oxidised indanthrone of high quality. A.T.P.

### Yellow Anthraquinone Vat Dyes

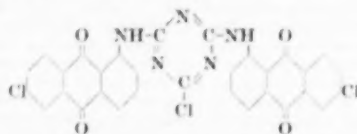
Ciba

BP 831,880

Yellow vat dyes of very good fastness, especially to light, for dyeing and printing natural or regenerated cellulose, are of formula—



(A = anthraquinone nucleus bound in the  $\alpha$ -position to the -NH group, and contains in at least one  $\beta$ -position of the benzene nucleus not bound to the -NH group, Hal or Alk of  $\geq 4$  C; X = primary amino, which may be subat. by at least one alkyl or non-vatable aryl residue, especially a benzene residue). They are obtained by condensing 1 mol. of cyanuric halide with 2 mol. of an amino anthraquinone, and then reacting the product with at least 1 mol. of  $\text{NH}_3$  or an aliphatic or non-vatable aromatic (especially benzene) amine. The aminoanthraquinones preferably contain  $\text{CH}_3$ , and especially Cl, in the 6- and/or 7-positions and mixtures of aminoanthraquinones may be used. Thus, 1-amino-6-chloroanthraquinone is refluxed in nitrobenzene in presence of HCl with cyanuric chloride to give the yellow vat dye—



A golden-yellow dye results by condensation of this with e.g.  $\text{NH}_3$  or  $\text{NH}_4\text{C}_2\text{H}_5$ . A.T.P.

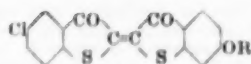
### Asymmetrical Indigoid Dyes

Ciba

BP 831,810

The title compounds—





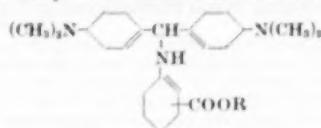
(R = Alk of 2-4 C) are obtained by condensing a 5-chloro-3-hydroxy- with a 6-alkoxy-3-hydroxythionaphthene, either of which may contain a reactive substituent in the 2-position. The dyes are reds of very good fastness and may be used on most fibres, especially cotton; they are very suitable for printing. Compared with the isomeric dyes of GP 627,903 they are more level dyeing and have better wash fastness. Thus, 5-chloro-3-hydroxythionaphthene (18-5) is condensed at 80-90°C. in chlorobenzene (500) with the 2-(*p*-dimethylamino)-anil of 6-ethoxy-3-hydroxythionaphthene. The dye (R = C<sub>2</sub>H<sub>5</sub>) separates and when printed on cotton by the potash printing process, gives a clear red of excellent fastness. The same dye is obtained from 6-ethoxy-3-hydroxythionaphthene and the 2-(*p*-dimethylamino)-anil of 5-chloro-3-hydroxythionaphthene. A.T.P.

#### Leucauramine Compositions

Caribonum

BP 831,852

New *ortho*- and *para*-carboxyphenyl-leucauramines (I) obtained by condensing Michler's hydrol with alkyl esters of *o*- and *p*-aminobenzoic acid are of formula—



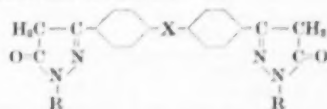
(R = Alk; -COOR is *o*- or *p*- to -NH). They are colourless and can be carried in a coating on a colourless transfer sheet material. When transferred to an acid copy sheet or otherwise subjected to slightly acid conditions they are converted into substantially lightfast colorants. The process is an improvement over conventional "carbon" and other colour transfer sheet materials, e.g., the colorant is only produced by the actual writing process and the transfer sheet material is substantially colourless. Thus, when one or more (I) are included in a transfer coating, and the coating, after drying or otherwise fixing upon the paper, is brought into contact with an acid coating containing, e.g. tannic acid and/or phosphotungstic acid, the leucauramine derivative is converted fairly rapidly into an intense blue colorant, the intensity of the colour increasing up to a maximum with time. A.T.P.

#### Bis-Pyrazolones and Derived Polypyrazolone Pigments

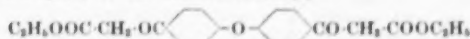
General Aniline

USP 2,903,461

Bis-pyrazolones of formula—



(X = O, S or SO<sub>2</sub>; R = H, Alk, aralkyl or Ar), are intermediates for polypyrazolone pigments. They may be obtained by condensing bis-keto esters with hydrazines. Thus, into a reaction vessel fitted with pH electrodes are charged ethyl acetoneacetate (85), ice and water (150) and a xylene solution (565 ml.) of diphenyl ether dicarbonyl chloride, equivalent to 76.3 g. of 100%. The pH is adjusted to 10.5-11.0 by running in 50% NaOH below 10°C., pH 11.0 is maintained by adding HCl whenever necessary. The mass is stirred at 10°C. for 30 min. and then allowed to come to room temperature in 1 hr. The aqueous layer is separated and treated with conc. NH<sub>4</sub>OH (50) and NH<sub>4</sub>Cl (50) for 1 hr. before a final addition of NH<sub>4</sub>Cl (50) and stirring overnight. Filtration gives a paste (236) of the bis-keto ester (I)—



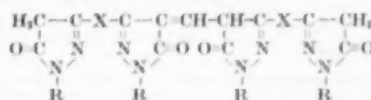
Crude I (216) is heated on a steam bath for 2 hr. with phenyl hydrazine (87) and the resulting dry reaction mass ground with methanol until washings are colourless. Recrystallisation from pyridine gives the title compound where X = O and R = phenyl (II).

USP 2,903,451

The polypyrazolones obtained by condensing 2 mol. of one of the above bis-pyrazolones with 1 mol. of a methyldene donor linking agent, e.g. chloroform, ethyl chloroformate or formamide, are oil- and water-insoluble yellow pigments. Thus, a ball-milled slurry of II above (25) is heated rapidly to reflux (165°C. rising to 195°C.) with formamide (800 ml.). After 12 min. the boiling liquor is filtered and the cake washed with formamide and then acetone until colourless runnings are obtained from both washes.

USP 2,903,452

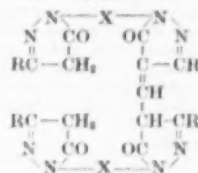
Polypyrazolones of formula (III)—



(X = a phenylene, naphthylene or biphenylene radical; R = H, Alk, benzyl, phenyl, naphthyl or biphenyl and may carry substituents) are oil- and water-insoluble yellow pigments. They are obtained by condensing 2 mol. of the bis-pyrazolones of USP 2,013,181; GP 625,813 and GP 650,558 with a methyldene donor linking agent (1 mol.), especially formamide. The crude products are preferably treated with H<sub>2</sub>SO<sub>4</sub> in a closed vessel to give purified pigments of improved strength, brightness and light fastness. Thus, the bis-pyrazolone (10) from phenyl hydrazine and diethylterephthaloyl acetate is heated with formamide (90 ml.) to 185°C. in 54 min. and kept at 185-187°C. for 45 min. The mass is filtered at 120°C. and the cake washed with formamide at 120°C. and then water to give III where X = phenylene and R = phenyl. The above product is improved by dissolving it (10) at < 30°C. in H<sub>2</sub>SO<sub>4</sub> (100 ml.) and stirring the paste of pigment sulphate for 4 hr. before leaving to stand overnight. The sulphate is filtered, washed with conc. H<sub>2</sub>SO<sub>4</sub> (25 ml.) and the cake slurried in distilled water and ice. The purified pigment (7-7) is brighter, stronger, and faster to light than the crude product or the pigments obtained by recrystallising the crude pigment or by chlorinating it.

USP 2,903,462

Yellow poly-pyrazolone pigments of formula—



(X = naphthylene, bi-phenylene or bis-phenylene methane; R = Alk or Ar) are obtained by condensing 2 mol. of the bis-pyrazolones of GP 264,287; GP 289,290; GP 515,782 and USP 2,538,180 with 1 mol. of a methyldene donor linking agent, especially esters of chloroformic acid. Thus, 1,1'-(bi-phenylene-4,4')-bis-(3-methylpyrazolone-5) is reacted with ethyl chloroformate to give the yellow pigment in which R = CH<sub>3</sub> and X = biphenylene.

A.T.P.

#### Finely Crystalline Dioxazine Pigments

Gy

BP 831,243

Insoluble dioxazine dyes are rendered softer and of stronger colour by grinding them with a salt which is harder than the dye and which can later be removed by a solvent. The grinding is carried out in presence of a solid or liquid, non-acid reacting organic solvent. Thus the dye obtained by condensing 2 mol. 3-amino-N-ethylcarbazole and 1 mol. tetrachloroquinone (30) is ground with anhydrous CaCl<sub>2</sub> (90) and xylene (5) in a ball mill for 60 hr. It is then pasted in water (500) and conc. HCl (10), steam distilled and the pigment filtered off, and washed free from salt and dried at 60°C. This yields a violet powder of good colour strength and particularly suitable for dyeing polyvinyl chloride.

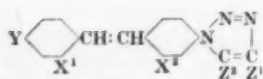
C.O.C.

#### Stilbene Triazoles—Fluorescent Brightening Agents and Dye Intermediates

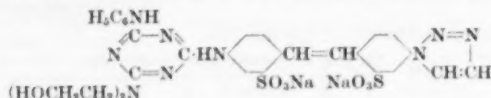
FBy

BP 829,788

Compounds of formula—



(X¹ and X² = sulphonic or carboxylic acid groups; Y = Hal, NO₂, acylamino or a subst. triazylamino group attached via a N atom, a subst. or unsubst. triazyl attached via a N atom, or arilo-triazoyl attached via one of the three N atoms; Z¹ = H, Alk, hydroxyalkyl, Ar or esterified carboxyl; Z² = H or Z¹) e.g.—



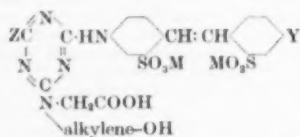
are intermediates for dyes and when they contain no NO₂ group are also fluorescent brightening agents applicable from aqueous or organic solution and in presence of detergents. C.O.C.

#### Fluorescent Brightening Agents

Fran

BP 830,613

Compounds of formula—



(M = monovalent cation; Y = triazylamino; Z = OH, NH₂, or Hal), e.g. N,N'-bis(2'',N''-carboxymethyl-hydroxyethylamino-4'',chloro-1'',3'',5''-triazyl)-4,4'-diaminostilbene-2,2'-disulphonic acid are fluorescent brightening agents applicable to a wide range of substrates particularly cotton and nylon. C.O.C.

#### 4-Methyl-7-dimethylaminocoumarin—Fluorescent Brightening Agent for Use in Perborate Compositions

American Cyanamid Co.

USP 2,903,430

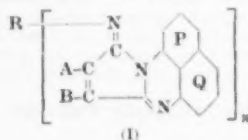
4-Methyl-7-dimethylaminocoumarin like its diethyl homologue is an excellent fluorescent brightening agent for protein and synthetic fibres but has the great advantage that it is stable to perborate and/or other alkali components of conventional bleaching compositions. When mixed with such compositions even after long storage it neither tends to smelt nor to lose its brightening property. C.O.C.

#### Heterocyclic Pigments

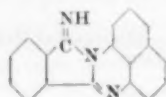
ICI

BP 830,403

Bright pigments of high tinctorial strength and stability to heat and light, and especially useful for colouring plastics, paints, varnishes, fibre spinning dopes, and artificial fibres, are of formula—



(R = Alk, cycloalkyl, aralkyl, Ar or a heterocyclic radical; A and B = subst. or unsubst. hydrocarbon radicals or together form a homocyclic or heterocyclic ring, especially a benzene ring; n = 1-3; P and Q may carry substituents, e.g. halogen, alkoxy. They are obtained by condensing the intermediates of BP 799,352 (J.S.D.C., 74 (1958) 714) with amines or amine hydrochlorides, which may be mono-, di- or tri-amines of the primary alkyl, cycloalkyl, aryl, aralkyl or heterocyclic classes. Thus, 12-imino-phthaloperine (II) —



is heated for 2 hr. at 240-260°C. with aniline hydrochloride in nitrobenzene to give the reddish orange 12-phenylimino-phthaloperine (I where R = phenyl and n = 1). Similarly II with p-nitroaniline (reddish brown), dehydrothio-p-toluidine (red) and p-phenylene diamine (purple-red). A.T.P.

#### Copper Phthalocyanine (C.I. 74160)

General Aniline

USP 2,900,390

Cu phthalocyanine, obtained by conventional reaction of phthalic anhydride, a copper salt and urea in presence of a catalyst and solvent, is isolated in a high state of purity by reducing the temperature of the reaction mass to a minimum of 120°C., preferably 140-150°C., and then thoroughly mixing the cooled mass with water at < 50°C., preferably 50-85°C. (volume of water to reaction mass being < 4:1) and finally filtering off the pigment. Lengthy and expensive extraction processes are thus avoided and the product is in a high degree of purity. Thus, a mixture of phthalic anhydride (373), cupric chloride (70), urea (600), NH₄ molybdate (2) and trichlorobenzene (1500) is refluxed at 200°C. until reaction is complete. The mass is cooled to 140°C. and fed into a hammermill with 4 times its vol. of water at 50°C., agitated, filtered and the cake steam stripped to give a high quality Cu phthalocyanine. A.T.P.

#### Non-Flocculating Metal Phthalocyanine Pigments

Chemetron Corp.

USP 2,902,384

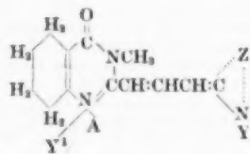
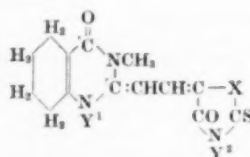
The tendency of compositions containing phthalocyanine pigments to form aggregates and settle out on standing is overcome by addition of an insoluble salt of a metal phthalocyanine sulphonic acid and an Al salt of an organic aromatic acid. Insoluble salts of a resin acid may be added also (cf. USP 2,526,345 (J.S.D.C., 74 (1958) 714; USP 2,099,689; USP 2,099,690). These non-flocculating compositions comprise a metal phthalocyanine pigment, 5-25% of an insoluble salt, e.g. Ca, Ba, of a metal (Cu) phthalocyanine mono-, di- or polysulphonic acid, 0.5-10% of an Al salt of an organic aromatic acid of 7-10 C, e.g. Al benzoate, and, optionally, > 5% Al resinate. Thus, all parts by weight, Cu phthalocyanine blue press cake (420 dry wt.), Cu phthalocyanine disulphonic acid press cake (46.5 dry wt.), a Na salt of a carboxylated polyelectrolyte dispersing agent, e.g. Tamol 731 (9.25), rosin (37.5), added in aqueous alkaline solution, sodium benzoate (24.5), hydrated Al sulphate (50), and BaCl₂ (15) are mixed thoroughly and washed with water to remove soluble materials. The resulting mixture is used as the basis of non-flocculating pigment compositions. A.T.P.

#### Cyanine, Styryl, and Merocyanine Dyes

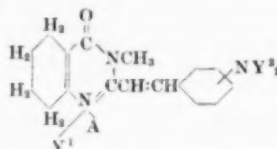
FH

BP 829,877

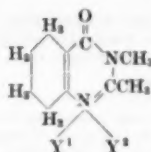
Dyes of formula—



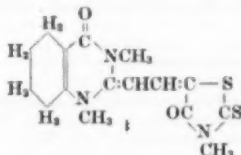
or



(A = inorganic anion; X = O, S or > N alkyl; Y¹ and Y² = CH₃ or C₂H₅; Z = atoms to complete a ring) are obtained by known processes from components of formula—



which are obtained by methylating 2-methyl-5,6,7,8-tetrahydroquinazolinol and quaternating the resulting 2,3-dimethyl-5,6,7,8-tetrahydroquinazolinol. Thus the red dye



is obtained by heating 2,3-dimethyl-5,6,7,8-tetrahydroquinazolinone (4) with *p*-toluene sulphonic acid, cooling and then refluxing with 5-acetanilidomethylene-*N*-methyl rhodamine in alcohol in presence of triethylamine.

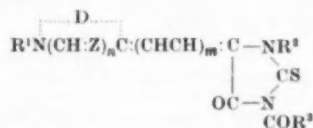
C.O.C.

### Merocyanine Dyes

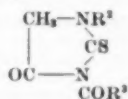
Ilford

BP 829,700

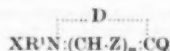
Dyes of formula—



( $R^1$  and  $R^2$  = same or different Alk, aralkyl or Ar;  $R^3$  = phenyl;  $Z$  = N or  $\text{CH}$ ;  $n$  = 0 or 1;  $m$  = 0, 1 or 2;  $D$  = atoms to complete a 5- or 6-membered nucleus) are obtained by condensing a compound of formula—



with one of formula—



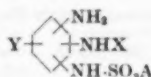
( $Q$  = thioether or acetanilido vinyl;  $X$  = acid radical) preferably in presence of a basic condensing agent. Thus the green 3-benzoyl-1-phenyl-2-thio-5-(3-methyl-2,3-dihydro-2-benzthiazolylidene) ethylidene thiohydantoin is obtained by refluxing the quaternary salt formed from 2-methylbenzthiazole and methyl *p*-toluene sulphonate with 3-benzoyl-1-phenyl-2-thiohydantoin in an alcohol-ether mixture in presence of triethylamine. C.O.C.

### Triamino-Benzene-*N*-Sulphonates—Brown Oxidation Bases

Fran

USP 2,906,587

The title compounds (I)—



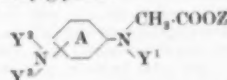
( $X$  = H or  $\text{SO}_3\text{A}$ ;  $A$  = H or an equivalent cation;  $Y$  = H, Hal, Alk or alkoxy), are used to prepare fast brown oxidation dyes for all fibres. Preparation of I is fully described, e.g. Na 1,2,4-triaminobenzene-*N*'-sulphonate by treating 2-nitro-1-amino-4-acetamido benzene with sulphuric chlorohydrin, followed by reducing the  $-\text{NO}_2$  group. Thus, cotton fabric is printed with Na-1,2,4-triaminobenzene-*N*'-sulphonate (44),  $\text{NaClO}_2$  (20),  $\text{NH}_4\text{Cl}$  (20), 20%  $\text{CuSO}_4$  (10), 1%  $\text{NH}_4$  vanadate (20), 20%  $\text{NH}_3$  (10) and water and starch thickener (876). After drying, the fabric is neutral steamed for 8 min. and soaped. This gives a dark brown print. A.T.P.

### Phenylglycine Oxidation Bases

Fran

BP 830,446

Substituted phenylglycines



( $Z$  = H or a monovalent cation;  $Y^1$  = H or  $-\text{CH}_2\text{COOZ}$ ;  $Y^2$  = H, Alk or  $-\text{CH}_2\text{COOZ}$ ;  $Y^3$  = H, Alk, Ar, or  $-\text{CH}_2\text{COOZ}$ ; the two substituents are preferably *meta* or *para* to one another, and  $A$  may be further substituted by e.g.  $\text{NH}_2$  and Alk) are used as rapidly developing brown to black oxidation bases for textiles. Thus, cotton is printed with a paste containing *p*-aminophenylglycine ( $Y^1, Y^2, Y^3$  and  $Z$  = H) (40),  $\text{NaClO}_2$  (30),  $\text{NH}_4\text{Cl}$  (30), 20%  $\text{CuSO}_4$  (20), thiodiglycol (50), 1%  $\text{NH}_4$  vanadate (20), 20%  $\text{NH}_3$  (40), and a starch or tragacanth thickener (770). The fabric is dried, steamed for 4–5 min. at  $100^\circ\text{C}$ . and soaped to give a deep brown of excellent general fastness, especially to washing. *p*-Phenylaminophenylglycine (obtained by treating *p*-aminodiphenylamine with monochloroacetic acid) similarly used gives a fast black.

A.T.P.

### Oxidation Bases

FBy

BP 830,851

Azomethines, obtained by treating primary aromatic amines with a heterocyclic or aromatic aldehyde, are used, either alone or with an aromatic hydroxy compound, as oxidation bases. Thus, a paste is made by dissolving the azomethine from 4-aminodiphenylamine and the Na salt of benzaldehyde *o*-, *m*- or *p*-sulphonic acid (100) in water (250), mixing the solution with diglycol (70) and 20% aq.  $\text{NH}_3$  (10) and stirring into a starch tragacanth thickener (500).  $\text{NH}_4$  oxalate (40),  $\text{NaClO}_2$  (40), and 1% aq.  $\text{NH}_4$  vanadate (820) are added and the paste made up to weight (1000) with water. Blacks of excellent fastness are produced on cotton, viscose and acetate rayons by printing with the above paste, steaming 5–10 min., rinsing and soaping. Printing pastes of this type have excellent stability in neutral or alkaline media.

A.T.P.

### Reactive Dyes containing a Sulphonethylenimine Group

ICI

BP 830,246

Reactive dyes are produced by introducing a sulphonethylenimine group into any water-soluble dye. They are especially suitable for application in aqueous medium to cellulosic materials in conjunction with an acid-binding treatment. Thus cotton cloth is padded with an aqueous solution of the dye *m*-aminobenzenesulphon-*N*-ethylenimine-1-acetylamine-8-hydroxynaphthalene-3,6-di-sulphonic acid, dried at  $50^\circ\text{C}$ . and then passed through an aqueous bath containing 1%  $\text{NaOH}$  and 30%  $\text{NaCl}$ . Finally it is steamed for 1 min., rinsed in 4% aq.  $\text{NaHCO}_3$  and then water, washed for 5 min. in a boiling 0.3% solution of an alkyl phenol-ethylene oxide condensate, rinsed and dried. The bluish red dyeing obtained has good fastness to washing.

C.O.C.

### Finely Dispersed Pastes of Water-insoluble Dyes

FBy

USP 2,902,385

Water-insoluble dyes are treated with < 10%, preferably 50–90%, of their weight of a polyglycol ether, if desired with addition of water or other suitable diluent. The ratio of the components is such that at the start of kneading it has viscosity < 2,000 cp. and preferably < 1,000,000 cp. The products rapidly disperse in either aqueous or non-aqueous media. Thus the dye 2,5-dichloroaniline-2'-3'-hydroxynaphthylaminobenzene (140) is kneaded with the condensate (100) of hydroxydiphenylbenzyl chloride and ethyleneoxide described in Example 1 of GP 824,949 and after 30 min. sufficient water added to yield a paste capable of flowing. The dye in the paste has uniform size of 0.3–1.0  $\mu$ .

C.O.C.

### Isolating Caramel Colouring Compounds from Caramelised Sugar

Union Starch &amp; Refining Co.

USP 2,902,393

The colorants are separated from acid proof type caramel colour syrup, e.g. by addition of a water-soluble alcohol. The uncaramelised sugar is recovered and re-caramelised under such conditions that the impurity and ash content does not prevent production of a good acid proof colour syrup. When the ash content does exceed

this level it can be removed by ion-exchange methods or the syrup can be used to produce either brewer's or baker's type caramel colour syrups. The acid proof type has an isoelectric point at  $< \text{pH } 3.2$  and becomes increasingly electronegative as the pH rises, brewer's type has its isoelectric point at about  $\text{pH } 7.0$  and is electropositive down to low pH, baker's type has its isoelectric point at rather higher pH than the acid proof type, usually at  $\text{pH } 3.4$  and yields heavy precipitates with electro-negative colloids. C.O.C.

#### Water-dispersible Carotenoid Compositions

F. Hoffmann-La Roche & Co. BP 831,765

Compositions stable to air and moisture and readily dispersed in aqueous media are formed by dispersing a supersaturated solution of a carotenoid in an edible oil in a water-soluble gellable material, and then setting to produce a dry powder. C.O.C.

#### Calcium Carbonate (C.I. Pigment White 18)

Diamond Alkali Co. BP 832,829

A pigment of average particle size  $> 1 \mu$ , particularly useful in the paper coating and plastics industries is produced by mixing an aqueous solution of a Ca salt with stoichiometric excess of an aqueous solution of an ammonium carbonate of  $\text{NH}_4\text{CO}_3$  molar ratio of  $< 2$  and vigorously agitating the mixture while maintaining it at  $20-40^\circ\text{C}$ . A small amount of  $\text{CaCO}_3$  of average particle size  $0.03-0.15 \mu$  is added to either or both of the reactants or to the mixture. Finally the precipitated product is separated off and dried. C.O.C.

#### Precipitated Calcium Carbonate (C.I. Pigment White 18)

Solvay et Cie BP 831,921

A pigment of very small particle size particularly suitable for use with paper and rubber is produced by carbonating milk of lime, there being added to the liquor at any time before separating the pigment from it a soluble ionisable compound of Al, Mg, Va, Cr or ferrous iron, i.e. before or after carbonation. C.O.C.

#### Carbon Black Pellets (C.I. Pigment Black 6 and 7)

Columbian Carbon Co. BP 830,579

The pigment is formed by a dry process into pellets of bulk density  $< 20.5 \text{ lb./c.ft.}$ . The pellets are then moistened with water containing resin particles of size  $> 5 \mu$ , and a dispersing agent which is decomposed when the pellets are dried at  $> 212^\circ\text{F}$ . The resin must be one which is a hard solid at  $70-110^\circ\text{F}$ , but is soft and pliable at the temperatures used in dispersing the pigment in rubber. The pellets do not tend to crush or mat together under severe conditions of carriage and mechanical handling. C.O.C.

#### $\alpha$ -Ferric Oxide (C.I. Pigment Red 101)

Columbian Carbon Co. BP 830,108

$\gamma$ -Ferric oxide (C.I. Pigment Brown 6) is dispersed in an aqueous solution of a ferrous salt ( $0.1-0.5 \text{ mol./litre}$ ) containing an inorganic acid, e.g.  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ , and then heated at  $70-100^\circ\text{C}$ . until it is completely changed from the brown  $\gamma$ -form to the red  $\alpha$ -form which usually takes 4-6 hr. C.O.C.

#### Pure Iron Oxide Pigments (C.I. 77491 and 77492)

Northern Pigment Co. USP 2,904,402

Iron oxide of high reflectance, purity and uniformity is obtained by controlling the formation of the seeds in a Zoph type of lime process so that precipitated Ca salts, complex salts and oversized particles may be eliminated preferably before the pigment seeds are oxidised while in contact with metallic Fe in the pigment-forming stage of the process. Thus  $\text{Ca(OH)}_2$  (500 lb.) is added to water (3,000 gall.) in a wooden tank.  $\text{FeSO}_4$  (1,000 lb.) is then added in solution to form  $\text{Fe(OH)}_2$  pigment seeds as a suspension in aq.  $\text{CaSO}_4$ . About 500 lb. of seeds are formed and 900 lb. of  $\text{CaSO}_4$  precipitated.  $\text{FeSO}_4$  (2,000 lb.) dissolved in water (1,000 gall.) are then added and air bubbled through until yellow seeds of  $\text{Fe(OH)}_2$  are formed. If red seeds are desired then the second lot of  $\text{FeSO}_4$  is replaced by  $\text{Fe}_2(\text{SO}_4)_3$ . The  $\text{CaSO}_4$  in suspension is then removed by centrifuging until the  $\text{CaSO}_4$  is  $> 5\%$  on the weight of the ferric seeds. The seed suspension is then washed with water to remove the remaining  $\text{CaSO}_4$ . The resulting pigment seed free from  $\text{CaSO}_4$  is then placed in contact with scrap iron, the particle size of the final pigment being controlled by controlling the viscosity of the iron oxide mass during its formation, maintenance of

high viscosity tending toward slow formation of fine particles whereas low viscosity (obtained by addition of water) yields coarse particles. C.O.C.

#### Zinc Ferrite Pigment

Columbian Carbon Co. USP 2,904,395

$\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  in molecular proportions are formed into an aqueous slurry, 0.1-1% of  $\text{ZnCl}_2$  or other volatile chloride added, dried at  $100-125^\circ\text{C}$ . and calcined for 10-30 min. at  $750-1000^\circ\text{C}$ ., slowly cooled to  $400-500^\circ\text{C}$ . and ground. This yields a light yellow pigment free from water-soluble salts and exceptionally stable to heat, alkali, and acids. It is non-ferromagnetic and highly compatible with other non-ferromagnetic materials. C.O.C.

Colour Couplers (Gevaert) (IX p. 382)

Colour Couplers (ICI) (IX p. 382)

Salts of Arylguanidines with Aryldiazosulphonates or with Aryltetrazodisulphonates—Use in Diazotype and Lithographic Materials (IX p. 383)

### V—PAINTS; ENAMELS; INKS

#### Polyurethane Coatings (Chemistry and Fundamentals)

M. E. Bailey Off. Dig. Fed. Paint Varn. Prod. Cl.,

32 (Feb 1960) 197-202

A summary, without bibliography. J.W.D.

#### Baked Polyurea Coatings

G. A. Hudson, J. C. Hixenbaugh, E. R. Wells, J. H. Saunders, and E. E. Hardy

Off. Dig. Fed. Paint Varn. Prod. Cl.,

32 (Feb 1960) 213-221

Coatings are formed by reacting a diurethane (produced by treating tolylene di-isocyanate with 1-pentanol) with amine-bearing resins [Versamids (General Mills)] at an elevated temp. They show good adhesion to metal, flexibility, good resistance to acids and alkalis, and to immersion in water. The coatings can be applied from stable, one-component, water systems, and are suitable for use as industrial primers or one-coat protective paints. J.W.D.

#### Urethane Coatings from Castor Polyols

T. C. Patton and H. M. Metz

Off. Dig. Fed. Paint Varn. Prod. Cl.,

32 (Feb 1960) 222-229

The use of castor polyols in the preparation of urethane coatings is discussed for both pre-polymer and polyisocyanate type systems. Selection of raw materials, proportions of reactants, processing conditions, and the importance of the preparation of the substrate are dealt with in detail. J.W.D.

#### Di-isocyanate Adduct Coatings Based on Castor Oil

G. C. Toone and G. S. Wooster

Off. Dig. Fed. Paint Varn. Prod. Cl.,

32 (Feb 1960) 230-241

Transesterification of castor oil with polyols of low mol.wt. reduces the average distance between OH groups in the molecule; seven polyols are discussed in this connection. Adduct coatings of these products with tolylene di-isocyanate have, by virtue of the tighter cross-linking of the polymer, increased tensile strength, faster drying times, greater hardness, improved solvent resistance, and lower moisture permeability than coatings based on unmodified castor oil. J.W.D.

#### Reactions of Isocyanates with Drying Oils

G. Wilson and J. M. Stanton

Off. Dig. Fed. Paint Varn. Prod. Cl.,

32 (Feb 1960) 242-250

Urethane oils prepared from alkali-refined linseed and soyabean oils exhibit superior drying and film-hardness properties to those prepared from pre-bodied oils, but paints based on these vehicles are not differentiated by Weather-Ometer tests. Paints prepared with urethane oils based on alkali-refined linseed oil compare well in performance characteristics with a long-oil soyabean alkyd in outdoor exposures. Film properties of nine urethane oils prepared with various ratios of three different polyols are described. A wide range of film properties may be obtained with urethane oil products depending upon the choice of polyol and the relative proportions of drying oil, polyol, and di-isocyanate used. J.W.D.



**Polyether Polyols in Urethane Coatings**

A. Damusis, J. M. McClellan, and K. C. Frisch

*Off. Dig. Fed. Paint Varn. Prod. Cl.*  
32 (Feb 1960) 251-272

One- and two-component urethane coatings have been prepared by reacting a series of new polyether polyols with tolylene diisocyanate; simple and polymeric diols, triols, and tetraols were included. Polymerisation conditions were controlled to yield isocyanate-terminated (IT) and OH-terminated (OHT) intermediates with an ordered structure. Each IT intermediate was cross-linked by reaction with moisture, simple polyols, or OHT intermediates to form cured coatings. Several important physical performance properties were measured, and interesting relationships were found between these and the structure, the chemical composition, and the equivalent wt. of the raw materials used; these latter characteristics of polyols used in IT pre-polymers and cross-linking agents affect the flexibility, impact- and abrasion-resistance, and solvent-resistance of the coatings. Those cured with moisture tend to be harder and more solvent-resistant than those cured with polyols, when based on the same IT pre-polymer. A wide variety of combinations of coating properties was obtained by the use of simple or polyurethane polyols as cross-linking agents. When present in the cross-linking agent, tertiary amine *N* accelerated the hardening rate of the coatings and imparted a high degree of hardness, impact-resistance, and toughness. Polyether urethane coatings, appropriately formulated, appear to be of interest for: clear varnishes for protecting wood against exterior weathering or interior usage; concrete finishes for moisture-proofing and surface finishing; protection of metals against corrosive conditions; and lacquers for the protection and decoration of rubber, leather, and plastic products. There is a short bibliography of test methods for urethane coatings. J.W.D.

**Statistical Studies on One-package Polyurethane Surface Coatings**

S. N. Glasbrenner, B. Golding, and L. C. Case

*Off. Dig. Fed. Paint Varn. Prod. Cl.*  
32 (Feb 1960) 203-212

Four systems yielding surface coatings, and based on polyethers and polyisocyanates, have been formulated and studied. Two of them, one-package systems, one cured by reaction of the film with atmospheric moisture, the other by baking, have been investigated in detail. The relationships of film hardness and toughness to formulation variables are determined. Hardness may be predicted if the mean mol.wt. is known. J.W.D.

**A Flow Equation for Pigment-Oil Dispersions of the Printing-ink Type**

N. Casson

*Rheol. Disperse Systems, Proc. Conf. Univ. Coll. Swansea*,  
(1957) (Pub. 1959) 84-104  
*Chem. Abs.*, 54 (25 Feb 1960) 3989

Shear sensitivity of a flocculated dispersion can be expressed by the relation  $S^{0.5} = k_0 + k_1 D^{0.5}$  ( $S$  = applied stress;  $D$  = shear rate;  $k$  = constant). C.O.C.

**Some Measurements on Pigment-Plasticiser Dispersions**

E. Bantoft

*Rheol. Disperse Systems, Proc. Conf. Univ. Coll. Swansea*,  
(1957) (Pub. 1959) 105-126  
*Chem. Abs.*, 54 (25 Feb 1960) 3989

Three types of flow were observed when pigment pastes in tritolyl phosphate were sheared: true plastic (Bingham), plastic-thixotropic, and the type described by Casson (cf. preceding abstract). Some pastes seem to exhibit a negative Weissenberg effect. C.O.C.

**SABS 15/6/30 Standard Test Methods for Paints**

A South African draft standard now obtainable from the South African Bureau of Standards or the British Standards Institution. The methods specified are: Method 139 Wet film thickness; 140 Dry film thickness (measured by means of a mechanical type gauge); 141 Dry film thickness (measured by means of a magnetic flux type gauge); 142 Sanding properties of paint films; 143 Dry abrasion resistance of paint films; 144 Dirt retention of paint films; 145 Flexibility of paint films; 146 Impact resistance of paint films; 147 Scratch resistance of paint films; 148 Drying time of paint films. Storage stability of paint, varnish and lacquer; 149 Skinning test, 48 hr;

150 Short term: 30 days; 151 Long term: 6 months; 152 Consistency of paints: measured by means of a Krebs-Stormer viscometer (without stroboscope); 153 Consistency of paints: measured by means of a Krebs-Stormer viscometer (with stroboscope); 154 Colour of paint films, visual comparison; 155 Salt fog resistance of paint films; 156 Natural weathering resistance of paint films; 157 Humidity resistance of paint films. C.O.C.

**Model Experiments on the Re-wetting of Chalked Paints**

F. R. Eirich and R. Lauria

*Off. Dig. Fed. Paint Varn. Prod. Cl.*  
32 (Feb 1960) 183-195

Chalked paint is considered as a mixture of loose pigment and disintegrated, cross-linked vehicle. Re-wetting is studied via adsorption isotherms of wetting agents and/or polymer on chalk dust. Fine beads of cross-linked acrylic copolymers (eleven types were studied) and a special titania (C.I. 77891) were used as models for the dust. The polar wetting agents examined adsorbed, at best, only weakly on to either form of dust; they are probably unsuitable for re-wetting. Water-soluble acrylic polymers adsorb very well on polymer beads and penetration continues over a period of time. Polymer adsorption on to anatase titania is less strong but is still substantial. Water-soluble polymers or colloids appear the most promising for re-wetting purposes. J.W.D.

## PATENTS

**Metallic Zinc Paint**

C. P. Healy

BP 831,163

Paint formed by mixing Zn dust (C.I. Pigment Metal 6) with aqueous K phosphate and a soluble chromate or dichromate at pH < 8, does not set prematurely, has satisfactory adhesion and abrasion resistance and neither blisters during setting nor leaves dry non-adherent powder after setting. C.O.C.

**Water-base Paints pigmented with Zinc Oxide (C.I. Pigment White 4)**

B. F. Goodrich Co.

USP 2,904,526

An aqueous solution or solution/dispersion of a zinc-ammonia-polymer complex forms a film which is highly insoluble after air drying for a short time at ordinary temperatures. A copolymer of ethyl acrylate, acrylic acid, and methacrylic acid (89:5.5:5.5) (7 g.) is ball-milled with 25%  $\text{NH}_4\text{OH}$  (2) and water (61) to form a low viscosity, clear solution. To this is added ZnO (2) and the mixture ball-milled to yield a milky white product somewhat less viscous than the original solution. When spread on a glass plate a clear, smooth, almost invisible film is deposited which is neither loosened nor dissolved by prolonged soaking in water. A pigmented coating composition is obtained by adding rutile  $\text{TiO}_2$  (15) to the above mixture and ball-milling for < 24 hr. The composition thus contains 71% by weight on solids of ZnO and  $\text{TiO}_2$  and is completely stable when escape of ammonia is prevented. Spread on wood, glass, paper, and steel it forms smooth lightly adherent, hard coatings on air drying. Though less viscous than conventional latex paints it has good covering power and fair brushability. C.O.C.

**Stabilised Vehicles for Leafing Aluminium Coatings**

Reynolds Metal Co.

USP 2,904,525

Incorporating an organic salt of a saturated fatty acid of 12 C, e.g. diethylamine stearate, in paints based on a hard-setting resin and leafing aluminium (C.I. Pigment Metal 1) greatly retards destruction of the leafing properties of the pigment. Preferably the salt is added to the vehicle before the pigment. C.O.C.

**Coating Compositions**

Midland Silicones

BP 830,310

Addition of 0.01-5.0% by weight of monopropylpoly-siloxane imparts good flow properties to paints and lacquers, inhibits floating, flooding and silking, and deters foaming or bubbling during the mixing of the paint or lacquer. This addition does not interfere with the wettability of the coating finish. C.O.C.

**Craze-resistant Methyl Methacrylate Lacquers**

DuP

BP 831,042

A mixture of a solvent and (A) polymethyl methacrylate of relative viscosity 1.117-1.196 (40-75 parts by wt.), (B) plasticiser (0-25), (C) lacquer-grade nitrocellulose (5-20), and (D) polyester (20-50) obtained by

heating 1 mol. of an aliphatic dicarboxylic acid of 4–10 C or its acid chloride or anhydride with < 1.5 mol. of a bisphenol or bisphenol acetate, yields films which on stoving become very resistant to crazing. C.O.C.

CDC 13 (1029) Dye, Ink Blue, for Ink Industry  
CDC 13 (1030) Dye Methylene Blue, for Ink Industry  
(IV p. 370)

Application of Chlorosulphonated Polyolefin Polymer Coatings (XIII p. 387)

## VI—FIBRES; YARNS; FABRICS

### Changes of Crystallinity in Cellulose on Treatment with Aqueous Caustic Soda

B. Gohlke and C. Müller-Genz

*Faserforsch. und Textiltech.*, 11 (Jan 1960) 31–43  
Cellulose samples were pre-treated with aqueous caustic soda of differing concentration at 20–70°C. Crystallinity was estimated by the iodine sorption method or by hydrolysis and successive treatment with dilute solutions of increasing concentration. W.R.M.

### Tryptophan in Wool. I—Determination of the Tryptophan Content of Wool

D. R. Graham and K. W. Statham

*Text. Research J.*, 30 (Feb 1960) 136–139  
The tryptophan content of various wool samples and various keratins has been determined by applying the method of Spies and Chambers (*Anal. Chem.*, 21 (1949) 1249). Values for the root ends of a number of samples of wool were about 1%, the amount varying with the fibre quality. The tryptophan content of various keratins varied from 0.52–1.14%. P.G.M.

### Chemical Attack of Textile Fibres. II—Protein Fibres: (A) Wool

F. O. Howitt

*J. Textile Inst.*, 51 (March 1960) p 120–p 140  
An explanatory paper especially designed for the student and those having little knowledge of the subject. It reviews in a readily understandable manner the whole of existing knowledge in this field. C.O.C.

### Variation of Double Refraction on Heating and Cooling High Polymeric Fibres

A. Möhring and G. Duwe

*Faserforsch. und Textiltech.*, 11 (Jan 1960) 7–15  
Changes in the double refraction of Perlon fibres during heating and cooling have been studied, using fibres at different stages of extension from undrawn to highly drawn and after tempering at different temperatures. Double refraction varies little on heating until the temperature is above ca. 100°C. after which it increases but falls when the temperature is above ca. 200°C. On cooling double refraction appears to increase to a limiting value considerably above that before heating. Drawing increases double refraction and so does tempering, the increase due to the latter effect being apparently greatest when the increase in length due to drawing is about 100%. The results are discussed in terms of fibre structure. W.R.M.

### Shrinking of Polyester Fibres

H. Ludowig, H. Ramm, W. Roth, and E. Hannes

*Faserforsch. und Textiltech.*, 11 (Jan 1960) 15–21  
Shrinkage may be prevented by hot stretching and fixing under tension. Shrinking, at a given temperature, is greater if water is present. Damage may occur at temperatures of 140°C. and above, particularly if water is present. W.R.M.

### Static Electricity in Textiles

H. vom Hove *Textil-Rund.*, 15 (March 1960) 109–121

The importance of static increased with the introduction of the modern hydrophobic fibres which are practically non-conductors and therefore able to acquire high electric voltage. The different theories of how static is generated in textiles are discussed and some simple experiments to demonstrate the effect of static are described. Factors influencing the magnitude of the electric charge and their mode of action are explained and it is shown how static can interfere with processing at different stages of textile manufacture. Methods (physical and chemical) to counter-act static are described as well as instruments for the evaluation of anti-static preparations. According to American sources static can be much reduced or completely suppressed by spinning together polyester and

polyamide fibres. The opposite charges on the two fibres are supposed to cancel one another. Finally the connection between atmospheric electricity and the electric conditions of the room air is explained and use of static electricity in flockprinting described. W.M.

## PATENTS

### Regenerated Cellulose Fibres containing a Polyacrylamide

American Viscose Corp'n.

USP 2,901,813

Incorporation into a viscose spinning solution of an acrylamide of formula  $R^1R^2C=CR^3CO-NR^4R^5$  ( $R^1, R^2, R^3, R^4$  and  $R^5$  = same or different H,  $CH_3$  or  $C_6H_5$ ), e.g. a 50–50 copolymer of an acrylamide and acrylic acid, results in filaments which yield fabrics of improved resistance to crushing and of recovery from creasing. C.O.C.

### Resin Treatment of Rayon during its Manufacture

Courtaulds

USP 2,902,391

Rayon treated with an aqueous solution or dispersion of the precondensate of a resin while the filaments are still in the gel state and then the moisture content of the filaments reduced to below their normal water imbibition in the gel state and then cured had all the resin inside the fibres. C.O.C.

### Improving the Dyeing Properties of Synthetic Fibres by Treatment with Polyepoxides

Shell Development Co.

USP 2,903,381

Impregnation with an aqueous liquor containing a polyepoxide having several 1,2-epoxy groups and an amine catalyst followed by heat curing was used. Thus Orlon fabric impregnated with an aqueous emulsion of a polyglycidylether of epoxy equivalency 2–13, ethylene diamine and polyvinyl alcohol and then baked at 160°C. for 5 min. had a good handle, freedom from pilling and did not fray at cut edges. It was readily dyed with C.I. Direct Blue 71, C.I. Acid Red 5 or C.I. Disperse Blue 1 to give dyeings of good fastness to washing. C.O.C.

### Acrylic-Proteinaceous Fibre Blends giving Solid Dyeings with Neutral-dyeing Metal-complex Dyes

Dow Chemical Co.

BP 830,634

Blends of proteinaceous fibres and acrylic fibres containing a little N-vinyl lactam polymer readily give solid dyeings, when treated with neutral-dyeing metal-complex dyes by the same method as for the proteinaceous fibre alone. C.O.C.

Dyeing Tow of Synthetic Polymers (I p. 366)

## VII—DESIZING; SCOURING; CARBONISING; BLEACHING

### Modern Bleaching Methods with special reference to Chlorite Bleaching

P. Ferko

*Tintoria*, 56 (Jan 1959) 16–21

Hypochlorite, hydrogen peroxide, and chlorite bleaching are critically reviewed and compared on the basis of quantitative measurements. The following values were measured: whiteness, tensile strength, extension at break, loss of weight. Handle and appearance were assessed and comparative costs were estimated. Chlorite bleaching is in every respect superior except for cost but this is compensated for by the lower loss in weight which is of special interest to vertical concerns. Further, chlorite bleaching needs less supervision and is widely applicable. Introduction of the modern activators (esters of organic acids) and activators of the Stoffel type have greatly reduced risk of corrosion of apparatus and evolution of noxious fumes. W.M.

## PATENTS

### Bleaching Cotton with Sodium Hypochlorite and Hydrogen Peroxide

Allied Chemical Corp'n.

USP 2,903,327

The cloth is immersed for < 3 min. in a 0.05–0.30% aqueous solution of NaOCl at pH 9–12 and 5–45°C. in absence of carbonate ions. It is then transferred without any intermediate treatment into aqueous  $H_2O_2$  containing Na silicate at pH 10–12 and 0–80°C. The cloth is then squeezed to 80–120% liquor content and kept at 75–150°C. for 15–120 min. and finally washed off. The bleached cloth has high absorbency and brightness and low ash content and fluidity. C.O.C.

### Continuous Bleaching or Dyeing of Cellulosic Fibres

Smith & Nephew Textiles BP 829,835  
A carded web is wetted with an aqueous solution of a wetting agent and mangled to make it flat and strong. It is then impregnated with an aqueous bleach or dye liquor, mangled to a predetermined liquor content, passed through a heater to bring it to bleaching or dyeing temperature, plaited or piled in an accumulator and left there till bleaching or dyeing is completed. In the case of bleaching the web is finally given an alkaline boil before being rinsed and dried, in the case of dyeing it is only rinsed and dried. C.O.C.

## VIII—DYEING

### Adsorption of Dye Mixtures by Cellophane Sheet. I.—Temperature and Concentration Dependence of Adsorption from Binary Mixtures

Y. Horiki, Y. Tanizaki, and N. Ando  
Bull. Chem. Soc. Japan, 33 (Feb 1960) 163-169  
Chlorazol Sky Blue FF (C.I. Direct Blue 1) (I), Chrysophenine G (C.I. Direct Yellow 12) (II) and *p*-nitro-aniline  $\rightarrow \gamma$  acid ( $\alpha$ -coupled) (III) were dyed on Cellophane sheet at 50, 70, and 90°C. for 24 hr. in 2.0 g./l. salt soln. both alone and as binary mixtures. Amounts adsorbed were estimated from 25% pyridine soln. Reduction in amount of dye adsorbed from binary mixtures assumed to be caused solely by complex formation, i.e. the amount of dye available for adsorption is that amount not complexed. The instability constant of complex (I and II) was calculated from law of mass action and varied from  $4.7 \times 10^{-7}$  mol./l. at 50°C. to  $1.4 \times 10^{-8}$  mol./l. at 90°C. Instability constant of complex (I + III) could not be calculated since the composition was not constant. The amount of I adsorbed is dependent upon the nature of the 2nd component, the mole ratio of components in complex and instability constant. Reduction in the amount of I adsorbed from a mixture decreases as temp. increases because the instability constant increases. F.J.

### Remazol Dyes—II

H.-U. van der Eltz and F. Osterloh  
Melliand Textilber., 40 (Dec 1959) 1443-1448  
Discussion on the dyeing characteristics of Remazol dyes and how they are affected by e.g. dyeing time and temperature, dye liquor ratio, salt, alkali and different cellulosic fibres on which they are dyed. A.T.P.

### Solvent-assisted Dyeing of Wool

U. Einsele S.V.F. Fachorgan, 15 (March 1960) 206-212  
Cibacron (Ciba) reactive dyes are freely soluble in water but not in higher aliphatic alcohols and other organic solvents. The partition coefficient of several Cibacron dyes changes in favour of the organic phase after addition of Neovadin AN (Ciba) which forms a complex with the anionic reactive dyes. The author found that *n*-butanol and *n*-amyl alcohol assist in dyeing wool with reactive dyes in presence of Neovadin AN. The effect was most apparent when a saturated solution of alcohol in water was used. References are made to dyeing wool with 1:2 metal complex dyes from a 7% solution of *n*-butanol in water (Stevens and Peters). L.A.T.

### Dyeing Blends of Dacron Polyester Fibre and Cotton by the Du Pont Thermosol Process

J. J. Iannarone and W. J. Wygant  
Amer. Dyestuff Rep., 49 (8 Feb 1960) 50-54 (81-85)  
The Thermosol process is now in full scale use in several works in the U.S.A. for dyeing Dacron-cotton blends efficiently and economically. The most widely used procedure is to dye the Dacron first with disperse dyes by the Thermosol process and then vat dye the cotton by a conventional method. For some light to medium colours it may be possible to dye only the Dacron with disperse dyes by the Thermosol process. Selected vat dyes may also be used for both fibres. Dyeing both the Dacron and cotton in one heat-fixing operation using disperse and reactive dyes appears to be promising but a works procedure has still to be worked out. Blends of Dacron 64 and rayon can be dyed with the same dyes and methods as Dacron 64-cotton blends. C.O.C.

### Dyeing Dacron by Emulsions of Solvent Solutions of Dyes

R. J. Peirent, J. Casey, and G. Dadoly  
Amer. Dyestuff Rep., 49 (8 Feb 1960) 41-44 (72-75)  
Use of an aqueous emulsion of a solvent solution of a

dye is a very effective method of dyeing Dacron 54. The amount of disperse dyes taken up by Dacron from emulsified toluene solutions of these dyes by boiling for 1 hr. under atmospheric pressure was considerably larger than that from a normal aqueous dispersion at 250°r. under pressure. Dacron tops dyed by this method in a pilot plant were perfectly level and much deeper in colour than equivalent aqueous dispersion dyeings carried out at 250°r. C.O.C.

### Dyeing and Finishing Special Blends of Arnel and Acrylics and Arnel with Cotton in Circular Knit Application—I

R. E. Lacy and J. A. Dayvault  
Amer. Dyestuff Rep., 49 (8 Feb 1960) 45-49 (76-80)  
A practical one-bath method of dyeing Arnel-Orlon blends is based on (1) use of selected neutral-dyeing cationic dyes, (2) use of Igepon T (G), (3) pH kept at 6.5-7.0, and (4) separate addition and dilution of cationic and disperse dyes.

*Ibid.*, (22 Feb 1960) 45-47 (119-121)  
Gives the latest recommendations of Celanese Corp. of America for dyeing and finishing Arnel-Orlon and Arnel-Acrilan blends. C.O.C.

### Dyeing of Synthetic Fibres. V—Dyeing of a Polyacrylonitrile (Nitron) Fibre with Vat Dyes

A. A. Kharkharov and V. F. Androsoy  
Tekhnol. tekst. prom., No. 4 (11) (1959) 115-120  
Study of the dyeing of Nitron with Soledon Brilliant Violet K (paste) (I) and Indigosol Red Brown Zh (II) under varying conditions of dye-, acid-, and electrolyte concn, temp., length of dyeing, and drying before dyeing shows that dyeing of Nitron with vat dyes is closely similar to the direct dyeing of cellulose. The general fastness properties of dyed Nitron are good (5 and more), except fastness to light (4 for I, 3 for II). Dyeing Nitron at 60 and 80°C. before dyeing does not affect colour strength and fastness. Final oxidation is done with a mixture of  $\text{NaNO}_3$  (0.2 g./litre),  $\text{H}_2\text{SO}_4$  (2.0),  $\text{CuSO}_4$  (1.0), and  $\text{CO}(\text{NH}_2)_2$  (1.0). G.J.K.

### Basacryl Dyes on Polyacrylonitrile Fibres

A. Würz Melliand Textilber., 40 (Dec 1959) 1433-1438  
The use of Basacryl dyes on acrylonitrile fibres of the Orlon 42 type, in particular, high bulk yarns, is described. A one-bath, one-stage dyeing process for acrylonitrile-wool blends is fully described and suggestions for dyeing acrylonitrile-cellulose blends given. A.T.P.

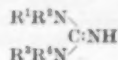
### Recent Advances in the Pressure Beam Dyeing of Synthetic Fibres

W. J. Newcomb and G. C. Ward  
Amer. Dyestuff Rep., 49 (8 Feb 1960) 55-58 (86-89)  
Recent advances include automatic heating and cooling, automatic pressure and flow control, automatic static pressure chamber, a closed pressurised expansion tank, a running wash system, and an automatic beam revolving device. General methods are given for dyeing standard fabrics including blends of synthetic and natural fibres. Suggestions are given for getting level dyeing, satisfactory fastness and proper setting of the fabric. C.O.C.

## PATENTS

### Dyeing Proteins and Nylon

Deering Milliken Research Corp. USP 2,900,218  
Level dyeings are obtained with milling dyes if a compound of formula—



( $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  = H, monocyclic aromatic, aliphatic or cycloalkyl radicals;  $\text{R}^4$  = monocyclic aromatic, aliphatic or cycloalkyl radicals), e.g. sym. diphenyl guanidine, is present in the dyebath. C.O.C.

### Dyeing Polyester Film

DuP BP 830,064  
The film is coated with a disperse dye in an organic solvent and then heated at 150-200°C. until the dye is fixed. Thus oriented polyethylene terephthalate film 0.0005 in. thick was coated at 15 ft./min. with a suspension in methyl ethyl ketone of the yellow 3-nitro-*N*-phenylsulphanilamide and the pink 1-amino-4-hydroxy-2-methoxy anthraquinone with a 50 line/in. knurled roller. The coated film was passed through a dryer at 150°C. for



40 sec. This gave a golden film which could be slit and used as yarn. C.O.C.

#### Dyeing Films and Fibrous Materials

G. W. Kunsch

BP 830,348

The materials are treated with volatilised dyes under high vacuum, i.e.  $10^{-2}$ – $10^{-4}$  mm. Hg. Thus Perlon fabric on a roller is placed in a vacuum chamber at  $10^{-4}$  mm. Hg. where it is rewound on to another roller while being treated with vaporised Celliton Fast Blue B (C.I. Disperse Blue 14). Finally the fabric is sprayed with a thin layer of a polyurethane. The resulting coloration has good fastness properties. C.O.C.

Dyeing Tow of Synthetic Polymers (I p. 366)

Reactive Dyes containing a Sulphonethylenimine Group (IV p. 377)

Improving the Dyeing Properties of Synthetic Fibres by Treatment with Polyepoxides (VI p. 380)

Acrylic-Proteinaceous Fibre Blends giving Solid Dyeings with Neutral-dyeing Metal-complex Dyes (VI p. 380)

Continuous Bleaching or Dyeing of Cellulosic Fibres (VII p. 381)

Co-ordination of Amino Acids with Cationic Chromium (XII p. 385)

Dyeing and Impregnating Leather (XII p. 386)

### IX—PRINTING

#### Screen Printing with Acid and Direct Dyes by the Saicutex V Process

G. Campari

*Tintoria*, 56 (June 1959) 247–249

The article deals with the use of an emulsion thickener. Preparation of printing pastes (water-in-oil emulsions) with Saicutex V Thickener (S.A.I.C.A. Soc. An. Colori Affini, Milan) is described. Emulsions are produced with a homogeniser of the Eppenbach type and an oil content of 5–10% yields sufficiently high viscosities. Addition of salts to the aqueous phase can be made and the usual quantities of acetic or formic acid can be incorporated in the case of acid dyes. Factors affecting the viscosity of the emulsion are discussed, among them the surface tension of the aqueous phase, and it is pointed out that some commercial dyes contain solubilising or dispersing agents which decrease the viscosity. This effect can be successfully counteracted by adding other thickeners to the aqueous phase, Indalca gum being especially suitable. Some recipes are given. Several advantages are claimed for printing pastes so prepared: better levelness, sharper outlines; a smaller number of passages with the squeegee and less printing paste are required to cover a given surface area, as printing pastes prepared with Saicutex have no great tendency to penetrate the fabric. As a further consequence the back of the fabric remains practically clean and less frequent washing of the tables is required. Higher production can be obtained. Fixation of dyes is improved and steaming times can be shortened. Because of the better dye fixation and the low solid content of the thickener washing of the printed pieces is facilitated. As Saicutex V has a marked softening effect the handle is improved. W.M.

#### Printing with Cibacron Dyestuffs

H. Werdenberg

*Melliand Textilber.*, 40 (Dec 1959) 1451–1454

Cibacron dyes are printed by an emulsion process to give three-colour prints on textiles. The process enables production of homogeneous mixture colours with fine gradations to be obtained, thus permitting new pattern effects. A.T.P.

#### PATENTS

#### Printing and Illuminated Discharge Printing of Textiles

BASF

BP 829,936

Textiles made from all types of organic fibres are printed with pastes containing vat dyes and/or disperse dyes (the latter being resistant to reducing agents), thickening and swelling agents, a water-insoluble or sparingly soluble hydroxyalkyl sulphinate as the reducing agent, and an amine. Such pastes are stable, inexpensive and yield high colour value with vat dyes. Thus cotton cloth printed with a paste containing 5,5'-dichloro-7,7'-dibromindigo (2% paste) (100 parts), Ba hydroxymethane sulphinate (100), polyethyleneglycol (60), triethanolamine

(50), crystal gum thickening (1:2) (500), water (160), and Na benzyl sulphinate (30), dried, rinsed, developed at 50°C. with ammoniacal peroxide and soaped, has a blue pattern on a white ground. C.O.C.

#### Oxidation Base Emulsions

American Cyanamid Co.

USP 2,899,261

When printing with oxidation bases, e.g. Aniline Black (C.I. Oxidation Base 1), the drop in viscosity of printing pastes based on starch or other carbohydrates and difficulty of penetration, e.g. when printing acetate rayon, are overcome if most of the starch is replaced by an oil-in-water emulsion thickened with a little galactan, e.g. gum tragacanth, mannogalactan, e.g. guar gum, or a polyacrylamide. C.O.C.

#### Organic Amino Compounds for Resists under Reactive Dyes

ICI

BP 829,443

The material is printed with a resist paste comprising an organic amino compound, e.g. Na salt of sarcosine, and a thickening agent. It is then padded with a solution of a reactive dye and when the material is natural or regenerated cellulose it is also treated with an alkaline compound or one which gives rise to alkali on being heated or steamed. C.O.C.

#### Yarn and Fabric Printing with Vat and Sulphur Dyes

British Cotton Industry Research Association

USP 2,899,264

After being printed the fabric or yarn is passed around a series of heated rotating cylinders. It is held against each cylinder by a travelling band of fluid-tight material and passes directly from the surface of one cylinder to the next. The temperature of the cylinders and their speed are so regulated that the prints are fixed when the fabric or yarn leaves the last cylinder. C.O.C.

#### Printing with Vat and Sulphur Dyes

BASF

BP 829,177

A solution of an alkali metal or  $\text{NH}_4$  salt of a straight or branched-chain hydroxyalkyl sulphuric acid of 2–4 C is used as the reducing agent. Thus cotton cloth is printed with an aqueous paste containing C.I. Vat Yellow 1 with carob bean flour and wheat starch as the thickening agents and dried. It is then padded with an aqueous solution of K hydroxyethane sulphinate, NaOH and Na tetraborate, and while still moist exposed for 30 sec. to steam in absence of air or excess pressure at 108°C. Finally it is rinsed in running water at 20°C. for 2 min., oxidised with aqueous perborate at 95°C., soaped, rinsed, and dried. A brilliant yellow print on a white ground is obtained. The same result is got if instead of steaming the moist fabric it is passed for 25 sec. between a metallic surface at 110°C. and a rubber cloth at 80°C. C.O.C.

#### Preventing Tarnishing of Bronze Prints

British-American Tobacco Co.

BP 831,227

Impregnation or coating with a borate of sodium or potassium (2–6% anhydrous borate on the weight of cellulose) gives good protection against tarnishing of bronze prints subsequently applied. C.O.C.

#### Multicolour Printing on Continuous Metal Bands

A. V. Borch-Madsen

BP 830,994

The band is perforated along either edge and then passed successively between printing rollers each having a pair of sprocket rollers arranged at either side of it to hold the band against the printing roller. The band passes in a loop from one printing roller to the next, the loop being free so as to remove distortions in the band. C.O.C.

#### Colour Couplers

Gevaert Photo-Producten

BP 831,731

Derivatives of 1-hydroxynaphthoic acid anilides substituted (1) in the o-position of the anilide group by an alkoxy group containing an aliphatic straight chain of > 5 C (this imparts fastness to diffusion) and (2) a sulphonic acid group *para* to this alkoxy group, yield dyes having a favourable absorption curve for use in negative material. In addition the dyes have good transmission of green light. Emulsions containing such couplers have lower viscosity than emulsions containing other couplers having good transparency in the green and so are more readily applied as coatings. C.O.C.

#### Colour Couplers

ICI

BP 830,797

Compounds of formula—



A-NH-CO-CHR<sup>1</sup>-CHR<sup>2</sup>-COOY

(Y = H, Alk, cycloalkyl or aralkyl; R<sup>1</sup> or R<sup>2</sup> = H and the other = NR<sup>3</sup> acyl (R<sup>3</sup> = H, Alk, cycloalkyl, aralkyl or Ar) or —



(Z = ethylene, phenylene or tetrahydrophenylene); A-NH = residue of a colour coupler, e.g. 4'-methoxybenzoylacet - 4 - (β - stearyl amino - β - carboxy - n - propionyl amino)-2-methoxyaniline, when used as colour couplers lead to no discoloration of the dye image on exposure to light as unreacted coupler present is fast to light.

C.O.C.

### Salts of Arylguanidines with Aryldiazosulphonates or with Aryltetrazodisulphonates—Use in Diazotype and Lithographic Materials

General Aniline *BP* 830,306  
Arylguanidine aryldiazosulphonates are photosensitive solvent-soluble compounds having important applications in the diazotype and lithographic fields, particularly in the manufacture of paper and metal lithographic plates.

C.O.C.

### Preventing Scum Formation in Colour Photography Developers

Ilford *BP* 830,625  
Hydroxylamine and either ascorbic acid or a compound of a 4-aryl-2-oxytetriconic acid or 4-aryl-2-oxytetriconimide used together prevent scum formation in developers for 12 hr. or more whereas hydroxylamine alone has no such action and the others exert an effect for > 4 hr.

C.O.C.

### Mechanism and Kinetics of Oxidative Colour Coupling

(IV p. 371)  
Leucauramine Compositions (IV p. 375)  
Reactive Dyes containing a Sulphonethylenimine Group (IV p. 377)

## X—SIZING AND FINISHING

### Cotton Quality Study. IV—Resistance to Weathering of Cotton Yarns and Fabrics

J. W. Howard and F. A. McCord  
*Text. Research J.*, 30 (Feb 1960) 75-117  
Review of the literature, 352 references. C.O.C.

### Methods to Improve and Test Resilience of Cotton Pile Yarns in Soft Floor Coverings

E. Abrams, H. Cox, and G. Milner  
*Amer. Dyestuff Rep.*, 49 (25 Jan 1960) 33-38 (34-39)  
Various formulations of synthetic latex and dimethylol cyclic ethylene urea (D.M.E.U.) resin have been applied to cotton carpet yarns prior to the construction of carpets. A 60:40 mixture of butadiene-high acrylonitrile latex and D.M.E.U. resin formulation gave the best results. A modified method of test to measure resilience or recovery from deformation of carpets is given. P.G.M.

### Amendment No. 2 to BS 1118:1952. Shrinkage on Laundering of Woven Cotton and Linen Fabrics

British Standards Institution (published 30 March 1960)  
The title of the standard has been altered to: Determination of dimensional change on laundering of woven cotton and linen fabrics. The foreword has been completely rewritten and amendments made to Clauses 1, 2, 4, and 5. C.O.C.

### Recent Developments in Finishing of Blends

H. H. Latham  
*Amer. Dyestuff Rep.*, 49 (25 Jan 1960) 39-42 (40-43)  
An assessment is given of different resin treatments (made in presence of Zn(NO<sub>3</sub>)<sub>2</sub> with and without a metallic buffer) to improve the properties of cellulosic blends. Crease recovery angle, strength, and shrinkage tests have been made on the treated fabrics after washing. P.G.M.

### Felting of Wool in Concentrated Solutions of Electrolytes

D. R. Graham and K. W. Statham  
*Text. Research J.*, 30 (Feb 1960) 151-152  
The felting of wool in calcium chloride and zinc sulphate solutions of various concentrations and at different

temperatures has been investigated. The results support those of previous workers that felting is reduced when the water content of the solution is reduced. P.G.M.

### Reducing the Felting Power of Wool with Polyglycine from the Polymerisation of Thiazolid-2,5-dione

J. H. Bradbury and J. D. Leeder  
*Text. Research J.*, 30 (Feb 1960) 118-127

Reduction of the felting power of wool with the reagent is not possible from aqueous solution but can be obtained at > 40°C. from a range of organic solvents of low water affinity. The abrasion resistance of treated fabric is about 1.5-2.0 times that of the untreated but the cost would be prohibitive in practice. Descaling shows that most of the polyglycine is located in the scales; a thin surface layer can be seen under the electron microscope. It is suggested that polyglycine cannot be attached by covalent bonds but by inter-molecular hydrogen bonds, and it is most unlikely that spot welding of fibres with polyglycine is a contributing factor towards reduction of felting power. P.G.M.

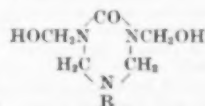
#### PATENTS

### Dimensional Stabilisation of Cellulosic Materials

Quaker Chemical Products Corp. *USP* 2,903,328  
The materials are treated with a polymeric acetal derived from an aldehyde and ethylene oxide, propylene oxide or butylene oxide. C.O.C.

### Crease-recovery Finish for Cellulosic Fabrics

Rohm & Haas *USP* 2,901,463  
Use of an aqueous solution containing 25-75 mole % of a compound of formula—



(R = 2-hydroxyethyl, 2-methyl-2-hydroxyethyl or Alk of 1-4 C) and a melamine, urea-NN'-ethyleneurea- or NN'-trimethyleneurea-formaldehyde condensate, gives good crease-recovery and dimensional stability without causing a smell, discoloration or loss of strength. C.O.C.

### Rendering Cellulosic Textiles Resistant to Creasing and Wrinkling

Olin Mathieson Chemical Corp. *USP* 2,904,387  
The cloth is impregnated with an aqueous solution containing < 4% by wt. of the condensate of < 4 mol. HCHO with 1 mol. dihydrazide of formula R<sup>1</sup>(CONHNH)<sub>2</sub> (R<sup>1</sup> = (CH<sub>2</sub>)<sub>3</sub>, e.g. oxalic dihydrazide). The liquor is at pH 5-7 and the pick-up 3-25% on the dry weight of the cloth. The impregnated cloth is then dried and baked. The finished cloth has excellent resistance to wrinkling and recovery from creasing and negligible chlorine retention when treated in solution containing active chlorine.

*USP* 2,904,388  
The dihydrazide used is of formula R<sup>2</sup>(CONHNH)<sub>2</sub> (R<sup>2</sup> = satd. chain of 2-6 C and is interrupted by 1 or 2 ether or thioether links), e.g. diglycolic acid dihydrazide. The condensate is prepared at pH 6-11 and gives the best results if the solution is stood for 24 hr. after the reaction. During this time the solution becomes more acid and can if desired be made neutral or alkaline before being used directly for padding on to cellulosic textiles.

*USP* 2,904,390  
The padding liquor is made by reacting formaldehyde with a hydrazide of formula R<sup>3</sup>(CONHNH)<sub>2</sub> (R<sup>3</sup> = H or subst. or unsubst. Alk; R<sup>3</sup> = H or R-CO-) e.g. diformic hydrazide. It yields a finish which neither retains chlorine nor picks up Cu from water containing traces of the metal.

*USP* 2,904,389  
A solid mixture of 1 mol. of a mono- or dihydrazide, 4 mol. HCHO (as paraformaldehyde), and 2-15% by weight of an oxide, hydroxide or carbonate of Zn or Mg, is stable even on long storage. For use it is mixed with 3-15 times its weight of water while maintaining the pH at 6-11 preferably 7-9, it is then brought to pH 7 with HCl before being padded on to the cloth. C.O.C.

### Mechanical Finish on Cellulosic Fabrics Impregnated with Dimethylol Ethylene-, Propylene-, and Butylene-ureas

Joseph Bancroft & Sons Co. USP 2,899,263

Use of dimethylol ethylene-, propylene-, and butylene-ureas in the production of durable mechanical finishes has several advantages over the use of resins. They are water soluble and readily react with the cellulose under the processing conditions without polymerising. Thus there is no tendency for deposits to be formed in the equipment, e.g. on a glazing roll. It also allows of much greater latitude in the amount of moisture that may be retained in the fabric during mechanical finishing and also in the quantity of material applied. The finish obtained is more durable than that obtained when thermosetting resins are used and there is less loss in strength during processing. C.O.C.

### Water-repellent Finish on Cellulosic Fibres by Treatment with Alkenylsuccinic Acids and Anhydrides

Armour & Co. USP 2,903,382

The fibres are impregnated with an alkenylsuccinic acid anhydride of 19–35°C and then heat cured. Thus cotton cloth is immersed in a solution of 17-pentatriacontenylsuccinic anhydride (2 g.) in toluene (100 ml.) for 5 min., air dried and baked for 15 min. at 115°C. The treated cloth shows excellent water repellency. C.O.C.

### Surface-cyanoethylated Cellulosic Textiles

Deering Milliken Research Corp. USP 2,904,386

Cellulosic textiles containing free hydroxy groups have applied to them 3–40% of acrylonitrile and < 5% of an aqueous solution containing < 5% of a strong water soluble base, and are then aged and finally acid scoured to remove the excess base. Thus desized and mercerised 40 oz. cotton cloth is passed successively over a pair of stainless steel rollers whose surfaces have been slightly dulled by being rubbed with fine sand-paper. Each roller is 4 in. in diameter and they are placed 4 in. apart. The cloth touches the top of each roller through an arc of about 20° and moves at 40 ft./min. The bottom of the first roller dips through an arc of about 90° into aqueous 10% NaOH containing 2% Na 2-ethylhexyl sulphate and its upper surface moves in the same direction as the cloth. The speed of the roller is adjusted so that the cloth takes up 20% by weight of the liquor. The second roller dips similarly into acrylonitrile and its speed is adjusted so that the cloth has a pick-up of 16%. Immediately after leaving the second roller the cloth is tightly wound, wrapped in a sheet of vinyl plastic and stored for 18 hr. It is then unwound, washed in 2% acetic acid containing 0.1% dodecyl benzene sulphonic acid, rinsed, and dried. C.O.C.

### Increasing the Tensile Strength of Textiles

A. C. Baggenstoss and C. P. Baggenstoss

USP 2,904,455

Increase of 65% in tensile strength of textiles, especially those of cellulose or modified cellulose, is obtained by treating them with a Diels-Alder condensate of abietic acid and a dienophilic amine. Thus abietic acid (120 g.) is slowly dissolved in dimethyl aniline (240) while keeping the mass at room temperature. After all the acid has been added the mixture is stirred for 2 hr. The product is isolated, dried, and sulphonated with oleum at 50°C. The product is then added to ethylamine (30), dissolved in dimethylaniline (120), and the mixture kept at 15°C. for 10 hr. The product is applied to the textiles in the same way as a size. C.O.C.

### Rendering Textiles Rotproof and Antiseptic

Gallowhur Chemical Corp. USP 2,899,340

The material is treated with an aqueous solution of a germicidal quaternary compound, e.g. 3,4-dichlorobenzylammonium chloride, and then with an aqueous solution of Na 2-mercaptobenzothiazolate. The resulting rot-proof finish has good resistance to bleaching, washing, and dry cleaning. C.O.C.

### Fire-retardant Finish for Cellulosic Materials

Dow Chemical Co. USP 2,900,279

The materials are impregnated with an aqueous solution of an alkylene polyamine phosphate or borate and then treated with acetic, oxalic or 2,4-dibromosuccinic acid. Thus cotton sheeting was immersed in a 24% aqueous

solution of 1 mole diethylene triamine and 1 mole phosphoric acid, drained and while damp treated in aqueous acetic acid and dried. When the finished cloth was exposed to a flame it was self-extinguishing and showed no after-glow. C.O.C.

### Non-slip Finish on Yarns of Nylon or other Synthetic Material

FBy BP 829,918

Yarns of nylon and other synthetic materials are rendered non-slipping, e.g. when made into nets, if they are treated with solutions of diisocyanates and/or polyisocyanates and dihydroxy and/or polyhydroxy compounds of mol.wt. > 500 and then, if desired, baked. C.O.C.

### Durable Stiff Finish on Polyamide Textiles

ICI USP 2,899,341

The materials are treated with an aqueous solution of an acrylic acid polymer, a polyhydric alcohol and, optimally, an acid catalyst, and then baked. Thus nylon twill impregnated with 76% of its weight of an aqueous solution containing 4.5% acrylic acid polymer and 1.5% glycerol, dried at 50°C. and baked at 150°C. for 30 min., receives a stiff crisp finish which withstands soaping at the boil. C.O.C.

### Heterogeneous Hydrolysis of Polyesters

FH BP 828,903

The polyesters are treated with aqueous solutions of inorganic alkaline splitting agents in presence of promoters providing cations of strong organic bases, until the desired loss in weight is achieved. Thus polyester yarn treated with 0.4% NaOH for 2 hr. at 60°C. lost 0.23% in weight, when 0.1% N-dimethyl-N-palm kernel fatty alkyl N-benzyl ammonium chloride was present as promoter then the loss in weight was 2.26%. C.O.C.

### Fabrics containing Bactericides

G. V. N. Morin BP 830,139

A carded web is printed with a non-ionic binding agent composed of a copolymer of < 70% vinyl acetate with an alkyl acrylate or methacrylate and is then treated with an aqueous solution of a quaternary ammonium bactericide, e.g. 0.1% aqueous diisobutylresorcyloxyethoxyethyl dimethylbenzyl ammonium chloride. C.O.C.

### Bonding, Coating, and Impregnating Polyester Fibres

ICI BP 828,922

The fibres or fabrics containing them are treated with polyesters softening at 140–230°C. and derived from glycols of formula HO(CX<sub>2</sub>)<sub>n</sub>OH (X = H or CH<sub>2</sub>; n = 2–10) and terephthalic acid, in presence or absence of another dicarboxylic acid. The process has many applications including bonding of polyester materials to themselves, stiffening, and water proofing. C.O.C.

### Coated, Impregnated or Bonded Fibrous Sheets

FBy and Carl Freudenberg BP 830,088

Products having good elasticity, even after dry cleaning, are obtained if the coating or bonding agent used is an emulsion of an elastomer which is as far as possible of straight-chain nature and shows little cross-linking. C.O.C.

### Finishing Blended-fibre Fabrics

Raduner & Co. BP 828,696

In fabric composed of fibre blends, one of the fibres can be accumulated, without undue loss of length, either on the surface or inside the fabric, by treatment with chemicals and/or heat so as to cause the fibre to be accumulated in the interior, but not on the surface, to shrink. The fabric is stretched during, or preferably after, this treatment and either before or after the shrinking agent has been inactivated. This stretching is such that the fabric is restored to its original dimensions. It is preferable that the stretched fabric, either in presence or absence of tension, is treated with an agent which confers dimensional stability on one or all the components of the blend. C.O.C.

### Direct Coating Tracing Cloth

Winterbottom Bookcloth Co. BP 828,195

A sheet of cured polyester and polyvinyl composition has embedded in it a filling sheet of textile material. The polyester has been rendered absorbent for water or water-miscible organic solvents by (1) use of N-vinyl pyrrolidone as the vinyl monomer, (2) use as the vinyl monomer of styrene having a cellulose ether dissolved in

it, (3) incorporation of an amino alcohol, or (4) incorporation of a polyhydric alcohol containing > 2 OH groups in an amount to ensure that only one of the hydroxyl groups reacts with the polyester compositions. The process described in *BP 806,912* (J.S.D.C., 75 (1959) 176) may be used to make these sheets. The finished sheet is capable of having directly applied to it a light-sensitive coating or ink or pencil markings. Thus a polyester resin obtained by condensing diethylene glycol with maleic anhydride is mixed with two-thirds its weight of *N*-vinyl pyrrolidone. Calendered bleached cotton cloth is dipped into this liquid composition, excess resin removed by doctor blades and the cloth combined with two sheets of regenerated cellulose sheeting which are wider than the cloth and fed on to a stenter enclosed in an oven at 180–250°r. The impregnated cloth is in the oven for 15 min. after which the cellulose sheeting is stripped off it. The resulting cloth has good transparency and can be coated with an acetone solution of a stabilised light-sensitive diazo compound. Prints made from the coated cloth have good clarity and fastness to washing. C.O.C.

#### Chromium Complexes of Fluorocarboxylic Acids as Oil Repellent Finishes

Deering Milliken Research Corp. *USP 2,904,571*  
Surfaces, particularly those of textiles, are made oil repellent by application of a Werner complex of trivalent Cr and a fluorinated carboxylic acid. In many cases the surface is also rendered water repellent. Thus chromic chloride hexahydrate (266) is melted in an open vessel and perfluoromyristic acid  $C_{13}F_7COOH$  (358) added, the mixture kept at 160°C. for 20 min. and then allowed to cool. The product is dissolved in warm ethanol (22), cooled to 5–10°C., filtered and evaporated to dryness to yield a water-soluble dark green product (370). This (300) is dissolved in isopropyl alcohol (700). To the hot solution (10) distilled water (90) is added. Woollen cloth impregnated with its own weight of this solution, dried at room temperature and stood for three days is highly repellent to both water and oil stains. C.O.C.

#### Finish to prevent Stockings slipping while being worn

A. J. Tlanicha *BP 814,722*  
Stockings are treated in a bath containing water (100 parts by wt.), highly polymerised polyisobutylene (1–2), softer polyisobutylene of lower mol.wt. (1–2), and polychloroprene or chlorosulphonated polyethylene (1–2), dried, and baked at > 150°C. This forms a thin flexible film on the threads which, however, does not cause them to stick together. It increases adhesion of the stocking to the leg during wear and so prevents the seam being displaced while the stocking is being worn. C.O.C.

#### Improving the Adhesion of Fibrous Materials to Rubber

Shell Development Co. *USP 2,902,398*  
The fibrous material is first treated with an aqueous medium containing a polyepoxide (epoxy equivalent > 0.20/100 g.) and a catalyst, dried, and finally treated with a liquid medium containing rubber and preferably, also, a fusible condensate of an aldehyde with a phenol, urea, melamine or ketone. The treated material when coated with rubber stock and vulcanised yields a product showing outstanding adhesion between the rubber and the fibrous material. C.O.C.

#### Backing Floor Coverings with Elastomeric Material

Witco Chemical Co. *BP 828,852*  
The material, e.g. carpet or matting, is coated on its back with a thin layer of a foamed elastomer, some or all of the cellular structure of the foamed elastomer being destroyed at atmospheric temperature during or after the coating is spread on the material. Finally the coating is dried and when necessary cured or gelled. C.O.C.

#### Book Binding Material

DuP *BP 829,674*  
A fibrous substrate is given a base coating comprising a vinyl chloride polymer and a 1,3-butadiene-acrylonitrile copolymer, and a top coating comprising a vinyl chloride polymer, a drying oil-modified alkyd resin and an aliphatic alcohol-modified urea-formaldehyde resin. The finished coated material is readily printed on by normal lithographic processes and is compatible with the adhesives and overprint lacquers used by bookbinders. In addition there is no danger that the plasticiser will tend to migrate. C.O.C.

#### Pile Fabric

Dike, Thompson & Sanborn *USP 2,902,397*  
A base material is treated so that it forms parallel projections or pleats. Rows of filaments are then placed across these projections and forced down into the depressions between the projections where they are held by adhesive. This forms a pile fabric with one series of loops in each depression and another series of loops over each projection. The pile may be kept in loops or cut. After the filaments have been placed in position the two walls of each depression are pressed together to bring them into intimate contact with the pile filaments and the adhesive. Finally the underside of the base material is secured to a backing coated with adhesive which comes into contact with the bottom edges of the pleats. C.O.C.

#### Water-repellent Finish (III p. 368)

1-Aziridinyl Phosphine Oxide or Sulphide Polymers for Rendering Hydrophilic Fibres Flame-resistant (III p. 368)

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

#### ISO/R66: Paper Vocabulary. First Series of Terms

British Standards Institution. Price, 13s. 6d.  
This ISO Recommendation includes terms and definitions relating to pulps and raw materials, processes, equipment and finished products. The definitions are all contained in BS 3203 (Glossary of paper, stationery, and allied terms). C.O.C.

#### PATENTS

#### Anti-foam Agents

Dearborn Chemical Co. *USP 2,903,432*  
The tendency of paper-making stock suspensions to foam is inhibited by addition of a still bottoms fraction recovered from the distillation of an aliphatic alcohol of 12–20 C, e.g. that described in *USP 2,070,597* and available commercially as Tagol brands (Archer-Daniels-Midland Co.). C.O.C.

#### Size imparting High Strength to Paper

Corn Products Co. *USP 2,903,391*  
The product obtained by etherifying a cereal starch with an alkylene oxide so as to form a hydroxyalkyl, partial ether of starch, adding a little borax and then drying the gelatinised combination to form a powder gives unexpectedly high strength to paper formed from pulp sized with this product. C.O.C.

#### Filled Paper

National Cash Register Co. *USP 2,902,399*  
Paper filled with a mixture of sodium aluminate and sodium silicate is particularly useful as a base sheet for colour-reaction with many organic colour-reactable compounds, e.g. with Crystal Violet lactone. C.O.C.

#### Chemical and Mechanical Deterioration of Wood in Contact with Iron (I p. 366)

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

#### Some Hide and Skin Curiosities

H. F. Green  
*J. Soc. Leather Trades Chem.*, 44 (Feb 1960) 83–88  
Examples of attack on hides by tick-birds, ants, and the case-making clothes moth, hyperkeratosis of hides, penetration of sheepskin by stick-grass thorns, unusual hair growth on hides associated with photo-sensitisation, unusual follicle grouping in camel hides, the difference in demodicosis in dogs from that in cattle and goats, and the resemblance between blemishes on hides from cattle which have recovered from lumpy skin disease and those on sheep- and goatskins after recovery from pox, are described and illustrated with photomicrographs.

J.W.D.

#### Co-ordination of Amino Acids with Cationic Chromium

S. G. Shuttleworth and R. L. Sykes  
*J. Amer. Leather Chem. Assoc.*, 55 (March 1960) 154  
Potentiometric titration curves and precipitation point estimations have been carried out on basic chromium



complexes prepared from sodium acetate, glycine,  $\beta$ -alanine,  $\epsilon$ -amino-n-caproic acid, and  $\alpha$ -,  $\beta$ -, and  $\gamma$ -amino-butyric acids. The conclusions drawn are: at pH 2.50–3.82 and using 1–3 moles acid per mole chromium, the amine groups are free and not attached to the chromium complex; direct estimations of the approximate amounts of free acids are possible and show no evidence of specific combining proportions over the above range; the general quantitative and stability patterns show a reversible mass action relationship with a trend favouring the amino acids of higher  $pK_1$  values, which is the opposite to that which would be expected if chelation of the amine group was occurring in the  $\alpha$ - and  $\beta$ -amino acids. P.B.S.

#### Mechanical Properties of Vegetable Tanned Collagen Fibres

R. G. Mitton and F. R. Morgan

*J. Soc. Leather Trades Chem.*, **44** (Feb 1960) 58–82

Thin collagen fibres are relatively stronger than thick ones; the latter are more subject to splitting during tanning. Breaking load and breaking length are virtually unaffected by length or method of vegetable tanning but, with a loading rate of 6 g./min., the humidity at which testing is conducted has a significant effect. Strength reaches a flat max. at intermediate humidities and falls away on either side of this range. Heavy fibres have on average lower breaking extensions than the others. Extensibility is also affected markedly by humidity. Although vegetable tanning does not affect the strength of collagen fibres it does reduce their extensibility. J.W.D.

#### PATENT

##### Dyeing and Impregnating Leather

FBY

BP 830,841

Dyeings fast to dry cleaning and washing and which impart a good handle are produced simultaneously with a water-repellent finish if an insoluble or soluble dye is applied by spraying or dipping. The leather is treated before or after dyeing with a solution of a diisocyanate-modified polyhydroxy compound containing free OH groups together with a polyisocyanate in an organic solvent. Dyed leather of poor fastness to rubbing can be given greatly improved fastness to rubbing by spraying it with the above solution. C.O.C.

Apparatus for the Measurement of Shrinkage Temperatures of Leather (XIV p. 387)

### XIII—RUBBER; RESINS; PLASTICS

#### Source of Free Radicals in Solution. II—Polymerisation of Some Vinyl Monomers by Electrolysis

W. B. Smith and H. Gilde

*J. Amer. Chem. Soc.*, **82** (5 Feb 1960) 659–661

Electrolysis of aqueous solns. of potassium acetate in presence of vinyl acetate (I), methyl methacrylate (II), or vinyl chloride produced the respective polymers, recovered from the cell by solvent extraction. Electrolysis in an H-cell divided by a glass frit produced polyvinyl acetate only at anode. If potassium acetate-2- $C_{14}$  is used with either the (I) or (II) radioactive polymers are produced. Evidence suggests that acetoxy or methyl free radicals, produced during electrolysis, initiate polymerisation. F.J.

#### Concentration Gradients for Diffusion of Vapours in Polymers

D. Richman and F. A. Long

*J. Amer. Chem. Soc.*, **82** (5 Feb 1960) 509–513

A microradiographic technique is described by which the concn. gradients of methyl iodide in polyvinyl acetate film, above the glass transition temp., at 30° and 40°C. can be measured. Diffusion coefficients were calculated from the concn.-distance curves and integral diffusion coefficients compared with those obtained from rate of sorption measurements. Method shows that the assumption of an equilibrium concn. at the polymer surface is valid.

#### Concentration Gradients for Diffusion of Vapours in Glassy Polymers

*Ibid.*, 513–519

Methods similar to the above have been used to study absorption of methyl iodide vapour by polyvinyl acetate and cellulose acetate below the glass transition temps.

Both systems exhibit anomalous behaviour usually observed in diffusion of organic vapours into glassy polymers. The initial surface concn.  $C_0$  is commonly only a small fraction of the final equilibrium value  $C_{eq}$ . The surface concn.  $C_s$  varies initially with time in a linear manner and finally varies according to the equation—

$$C_s = C_0 + (C_{eq} - C_0) [1 - \exp(-\beta t)]$$

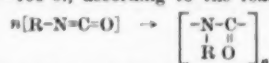
where  $\beta$  is obtained from  $K = \beta(C_{eq} - C_0)$   $K$  being the slope of the early  $C_s$  vs.  $t$ (time) plot. If this dependence on time and a constant diffusion coefficient are assumed it is possible to obtain explicit solutions of Fick's Law for diffusion into both an initially dry polymer and a polymer pre-equilibrated with a given amount of vapour. The resulting equations can explain the anomalous behaviour found in the former case and the two-stage behaviour in the latter. F.J.

#### Homopolymerisation of Monoisocyanates. I—Nylon

V. E. Shashouta, W. Sweeny, and R. F. Tietz

*J. Amer. Chem. Soc.*, **82** (20 Feb 1960) 866–873

A number of monoisocyanates have been polymerised at –20 to –100°C., according to the reaction—



in the presence of anionic catalysts, including NaCN in dimethylformamide, to give high mol.wt. linear polymers. The products, classified as 1-nylons, varied in physical properties depending upon the nature of group R which may be aliphatic or aromatic. The yield of the reaction product was increased by employing lower temp. but was limited by the decrease in solubility of the monomer. There appeared to be an optimum concn. of monomer and catalyst at which yield and mol.wt. were highest. The initiation, propagation, and termination mechanisms of polymerisation are discussed together with the properties, conditions of synthesis, and limitations of these 1-nylons. F.J.

#### Molecular Structure and Mechanical Behaviour of Macromolecules

T. Alfrey, E. F. Gurnee, and E. G. Bobalek

*Off. Dig. Fed. Paint Varn. Prod. Cl.*

**32** (March 1960) 360–387

Four structural factors; chemical composition, molecular architecture, crystallinity, and degree of swelling, determine the mechanical properties of a polymer. Each of these is briefly discussed and polymers are classified under the headings of linear polymers, cross-linked polymers and gels and other swollen structures. Mechanical and some physical properties of each class and sub-classes within it are discussed. The mechanical behaviour of a typical amorphous linear polymer is considered in terms of a mechanical model and the dependence of visco-elastic properties on molecular structure and temperature is discussed. Swollen polymers and gels and polyelectrolytes are briefly considered. A useful table is given showing expected changes in properties following structural or compositional changes in a polymer. W.R.M.

#### Synthesis of Grafted Copolymers by Reaction of Polymethylmethacrylate with Hetero-chain Polyesters

G. S. Kolesnikov and Tszén Khan-Min

*Izvestiya Akad. Nauk S.S.S.R., otdel khim. nauk.*

No. 7 (July 1959) 1336–1337

Grafted copolymers (GC) can be obtained by transesterification between polymethylmethacrylate and hetero-chain polyesters (polyethylene azelate and sebacate) in presence of an acid catalyst (HCl). It is concluded from X-ray and thermo-mechanical data that increased temp. of glassing of GC is caused by formation of ordered regions in which substituents are spaced out equidistantly along the main chain (pseudo syndiotactic regions of crystallinity); or, alternately, all substituents can be on one side of and coplanar with, the main chain (pseudo isotactic regions). Brief preparative directions are given. G.J.K.

#### PATENTS

#### Rendering Polyester Film adherent to Coatings and/or receptive of Ink or Pencil Marks

Winterbottom Book Cloth Co.

BP 830,777

Polyester film whose surface has been roughened with abrasives of particle size 5–50  $\mu$ . is receptive to clear and



legible marking with ink or pencil and/or firmly adherent to coatings of an organic hydrophobic film-forming material.

BP 830,778

The same effects are produced by treatment with an aqueous inorganic alkaline hydroxide so as to effect over-all pitting or corrosion of the film's surface.

C.O.C.

#### Siliceous Pigment-reinforced Synthetic Rubber of Reduced Permanent Set

Columbia-Southern Chemical Corpn. USP 2,903,439

Addition of sulphurised tall oil to synthetic rubber reinforced with siliceous pigments results in the high permanent set normally obtained on vulcanising being considerably reduced, usually by at least one-third.

C.O.C.

#### Suede-like Plastic Sheet

General Tire & Rubber Co. BP 833,416

A bare sheet is coated with a thermoplastic polymer material consisting mainly of a vinyl or vinylidene halide, a plasticiser, and a blowing agent. The coating is then heated to cause release of gas by the blowing agent and to fuse the coating. Finally the resulting cellular layer is abraded to produce a suede-like finish on it.

C.O.C.

#### Application of Chlorosulphonated Polyolefin Polymer Coatings

B. F. Goodrich Co. BP 831,846

One or more coats of a solution of the polymer are applied and are then vulcanised. Further coatings of the polymer solution are then given and they in turn are vulcanised. This prevents material migrating from the substrate into the top polymer coating and discolouring it.

C.O.C.

Polyurethane Coatings (Chemistry and Fundamentals) (V p. 378)

### XIV—ANALYSIS; TESTING; APPARATUS

#### Determination of $\alpha$ - and $\beta$ -Naphthol by their Infrared Absorption Spectra

Y. Nagase, S. Baba, and M. Suzuki

*Yakugaku Zasshi*, 79 (1959) 1145-8

*Chem. Abs.*, 54 (10 Feb 1960) 2661

Detection of  $\beta$ - in  $\alpha$ -naphthol was effected by the solution method with  $CS_2$  as the solvent and by the KBr pellet method, but  $\alpha$ - could not be determined in  $\beta$ -naphthol by the solution method because of the low solubility of  $\beta$ -naphthol in  $CS_2$ . There was no significant difference in accuracy between the two methods. The absorbance coefficient of the band at  $837\text{ cm}^{-1}$  ( $CS_2$ ) of  $\beta$ -naphthol in a mixture differs from that of  $\beta$ -naphthol alone and cannot be used as the key band.

C.O.C.

#### Infrared Analysis of Dyes. II—Malachite Green (C.I. Basic Green 4) and Green Food Dyes

M. Suzuki, E. Nakamura, and Y. Nagase

*Yakugaku Zasshi*, 79 (1959) 1209-1211

*Chem. Abs.*, 54 (25 Feb 1960) 3957

Examination of the infrared absorption curves of the green dyes permitted to be used as food dyes in Japan, viz. Guinea Green B (C.I. 42085), Light Green SF Yellowish (C.I. 42095) (I) and Fast Green FCF and of Malachite Green (II) showed that it is possible to detect up to about  $40\text{ }\mu\text{g}$ . by this method. Thus to determine II present in I use of the absorption at  $945\text{ cm}^{-1}$  as a key band for II and  $1024\text{ cm}^{-1}$  for I rendered possible determination of each component in a mixture of the two with a standard deviation (calculated by Youden's method) of 0.878 for I and 1.159 for II.

C.O.C.

#### Paper Chromatography of Direct Azo Dyes

G. Kiel and H. In't Hout

*Tex.*, 19 (March 1960) 131-141

Some commercial dyes were examined by ascending spot (A), descending spot (B), and descending band (C) chromatography. The dyes were used in a concn. of  $2\text{ g./l.}$  after drying over  $P_2O_5$  for 24 hr. at room temp. and under water-pump vacuum. The solvent was water with 10% alcohol (v./v.) and spots were made with a micropipette ( $8\text{ }\mu\text{l.}$ ), dried, and conditioned for 2 hr. over eluent vapour. Using pyridine-water (100/22 v./v.) as eluent and Whatman 52 paper, good chromatograms were

obtained of compounds belonging to different structure groups.  $R_f$  values varied according to the method used. In general C separated more components than A and B. Many direct dyes which according to the Colour Index are homogeneous, are actually mixtures, probably because of their complicated structure, method of preparation or by choice to get the desired hue. Using C it is possible to determine whether a direct dye is homogeneous or a mixture. C.I. Direct Brown 173, C.I. Direct Green 59, and C.I. Direct Blue 83 were found to be mixtures, while Benzo Brilliant Blue 6 BS and Chlorazol Sky Blue FF are not identical as indicated under C.I. Direct Blue 1. The identities of C.I. Direct Brown 5 and 95 and C.I. Direct Blue 71 were confirmed. 33 references.

R.A.

#### Chromatographic Data

*J. Chromatography*, 3 (Mar 1960) D6-D12

$R_f$  values of solvent dyes and food colours, presented in tabular form, from data given in *J. Sci. Ind. Res. (India)* 15C (1956) 186, 16B (1957) 131, 17B (1958) 304.

F.J.

#### Plastic Bag Technique for Paper Chromatography

D. Gunew *J. Chromatography*, 3 (Mar 1960) 281-3

To separate larger amounts of substances, with the same accuracy of definition, Whatman seed-test paper strip, around the top of which was heat-sealed a thin polythene tube, was used. The solution was applied through the tube, followed by eluent, as in column chromatography. Separation of 5 mg. samples of dyes in a mixture including *inter alia* Azo Geranine 2G (C.I. Acid Red 1) and Fluorescein (C.I. Acid Yellow 73) could be achieved.

F.J.

#### Apparatus for the Measurement of Shrinkage Temperatures of Leather

V. D. Barnett, R. G. Mitton, and F. R. Morgan

*J. Soc. Leather Trades Chem.*, 44 (Feb 1960) 88-92

Apparatus for simultaneously measuring the shrinkage temp. of any number of samples up to 32, operable up to  $125^\circ\text{C}$ ., is described and shown diagrammatically.

J.W.D.

#### Studies on Coal-tar Colours. XXIII—Identification and Determination of Triethylrhodamine and o-(2-hydroxy-4-diethylaminobenzoyl) Benzoic acid in Commercial Samples of D&C Red No. 19

C. D. Ritchie, J. A. Wenninger, and J. H. Jones

*J. Assocn. Off. Agric. Chem.*, 42 (Feb 1960) 720-724

Partition chromatography on silano-treated Celite revealed the presence of several subsidiary colours in commercial samples of D&C Red No. 19 (C.I. Basic Violet 10). Triethylrhodamine (C.I. Basic Red 8) was present in largest amount (1-2%). Some samples also contained 0.1-0.5% of the intermediate o-(2-hydroxy-4-diethylaminobenzoyl) benzoic acid.

J.C.F.

#### Photometric Determination of Frangula-emodin (C.I. 75440)

L. Krans

*Českoslov. farm.*, 8 (1959) 83-84

*Chem. Abs.*, 54 (10 March 1960) 5013

Reflux the sample (amount corresponding to 0.15 mg. of frangula-emodin) with 20% NaOH (20 mol.) for 20 min. and boil for a further 5-8 min. without condenser. Filter, treat the residue in the same way 3 times; cool and dilute the filtrates with NaOH to 100 ml.; determine the extinction in 5-cm. cells using the 853 filter (Pulfrich Photometer). The calibration curve in the concentration range of 0.1-0.3 mg./100 ml. of frangula-emodin is given.

C.O.C.

#### Gravimetric Estimation of the Density of Pigments by using a Pycnometer

K. Řeháček

*Chem. průmysl*, 9 (1959) 464-467

*Chem. Abs.*, 54 (10 March 1960) 5119

The gravimetric estimation of pigments was modified on the basis of a theoretical analysis of the accuracy of the pycnometric estimation of the  $d$  of powders in such a way that the  $d$  error is  $< 0.25\%$ . A tapered pycnometer with a large bottom was used. It enabled use of more pigment which is better deaerated in the liquid. The accuracy was checked with various pigments.

C.O.C.

#### Determination of Soluble Iron in Delustrated Acrylic Fibres

M. E. Gibson, D. A. Hoes, J. T. Chesnutt, and R. H. Heidner

*Anal. Chem.*, 32 (May 1960) 639-642

The sample is dissolved in dimethylformamide, the iron reduced to the ferrous state with hydroxylamine hydrochloride and a solution of 1,10-phenanthroline added to

form the coloured complex. The reflectance at 510-610 m $\mu$ , then gives, from the calibration curve, the amount of iron present.  $\text{TiO}_2$ , 0.5-1.0% of the fibre, has no effect on the results but for diluted solutions addition of  $\text{TiO}_2$  to give a concentration in the above range is necessary. Precision and accuracy are both about  $\pm 5-10\%$ . P.B.S.

#### Rapid Determination of the Aqueous Content of Textiles

M. Rösch *Melliand Textilber.*, 40 (Dec 1959) 1462-1464

Apparatus for the rapid determination of the grease content of textiles is described. Its use yields results in good agreement with those obtained by conventional extraction while the time required is much less. W.M.

#### Rotproofing of Cellulosic Textiles and their Testing. 3—Assessment of the results of the soil burial test using soils of different origin

W. Hausam and R. Rupp

*Melliand Textilber.*, 40 (Dec 1959) 1465-1468

Experiments with a cotton tent cloth of 420 g./m $^2$ , different types of soil and as preservative a mixture of pentachlorophenol and a proprietary product, Raluben, which is only sparingly soluble in water. This mixture gives sufficient protection and the type of soil is of little importance provided it is loose enough to be sufficiently active and the moisture content is such that the soil is just humid but not wet and tacky. W.M.

#### Determination of the Distribution of Curable Resins of Cotton Fabrics and Regenerated Cellulose Fabric with the Aid of Radioactive Isotopes

H. Enders and R. Zorkendorfer

*Melliand Textilber.*, 41 (April 1960) 462-468

Radioactive dimethylolethyleneurea was used. Measurements of the activity indicated that (a) uptake of resin is not the same on both sides of the fabric, (b) uptake of resin (measurement of the activity) is smaller than corresponds to the quantity of liquor taken up, (c) washing at the boil removes some resin from both fibres in the first wash. Repeated washing removes no more resin but in the case of regenerated cellulose causes loss of fibre material. W.M.

#### Development of a New Test Method for Colourfastness to Drycleaning

A. E. Johnson

*Amer. Dyestuff Rep.*, 49 (18 April 1960) 264-265

An account by its Secretary of the work of the AATCC Committee on Drycleaning Test Methods (RA 43) in developing Tentative Test Method 85-1960 (see next Abstract). C.O.C.

#### Colorfastness to Drycleaning

AATCC Tentative Test Method 85-1960

*Amer. Dyestuff Rep.*, 49 (18 April 1960) 265-266

A test for evaluating the effect of repeated drycleanings on the colour or colours of dyed and printed materials. It is not intended to be applied to metallic prints or for evaluating resistance of colours to spotting procedures used by drycleaners. C.O.C.

#### Dimensional Changes in Woven or Knitted Textiles (Excluding Wool)

E. Artin *Amer. Dyestuff Rep.*, 49 (18 April 1960) 266

The Chairman's report on the work of the AATCC Committee on Dimensional Changes in Textile Fabrics (RA 42) while developing AATCC Tentative Test Method 96-1960 (see following Abstract). C.O.C.

#### Dimensional Changes in Woven or Knitted Textiles (Excluding Wool)

AATCC Tentative Test Method 96-1960

*Amer. Dyestuff Rep.*, 49 (18 April 1960) 267-271

Four washing tests varying from very mild to very severe intended to cover the range of practical washing from commercial laundering to hand washing. C.O.C.

#### Relation and Felting Shrinkage of Woven or Knitted Wool Textiles

AATCC Tentative Test Method 99-1960

*Amer. Dyestuff Rep.*, 49 (18 April 1960) 284-285

Intended for materials containing  $\leq 50\%$  wool which have been rendered shrink resisting. It combines AATCC

Tentative Test Method 73-1953 (Shrinkage of Wool Hose: Accelerated Test), 74-1953 (Relaxation and Felting Shrinkage of Wool Knit Fabrics: Accelerated Test) and 41-1952 (Dimensional Changes in Wool Textiles: Accelerated Test) into one test method. C.O.C.

#### Identification of Resins in Fabrics

J. T. Marsh

*Text. Rec.*, 77 (May 1960) 72-74

A review of tests available for identification on the fibre of the commonly used resins. Acid or alkaline hydrolysis of the sample is followed by identification of the resin components. P.B.S.

#### Stain for the Microscopical Detection of Damage in Viscose Rayon

J. E. Ford *J. Textile Inst.*, 51 (April 1960) T 157-T 163

An aqueous solution containing 1% of Chlorazol Sky Blue FF (C.I. 24410) and 3% (by volume) of pyridine quickly stains the core at the ends of viscose rayon fibres. Where there is mechanical damage the core of the fibre is stained if the skin is broken. Materials to be examined are immersed in the stain for 30 min. at 25°C., blotted dry with filter paper, air dried and mounted in paraffin (n 1.47) for microscopical examination. Originally developed for detection of mechanical damage, the stain has proved useful in assisting recognition of other defects including abnormalities of fibre production and damage in chemically tendered fibres. The stain is intended for fibres of orthodox skin and core structure; it is unsuitable for high-tenacity fibres having no core. It is also unsuitable for use in presence of resins and these must be removed before the stain is applied to the fibre. Examples are given of the use of the stain on most common forms of damage finish in commercially defective materials. C.O.C.

#### Assessment of Light Fastness Exposures

K. McLaren

*J.S.D.C.*, 76 (April 1960) 232

Standard X-ray Diffraction Powder Patterns (IV p. 372)

SABS 15/6/30 Standard Test Methods for Paints (V p. 379)

Cotton Quality Study. IV—Resistance to Weathering of Cotton Yarns and Fabrics (X p. 383)

Methods to Improve and Test Resilience of Cotton Pile Yarns in Soft Floor Coverings (X p. 383)

Amendment No. 2 to BS 1118:1952. Shrinkage on Laundering of Woven Cotton and Linen Fabrics (X p. 383)

## XV—MISCELLANEOUS

### Note on Recent Demonstrations of Colour Mechanisms

S. Beig and J. Forkner

*J. Opt. Soc. Amer.*, 50 (April 1960) 394

Repetition of Land's work (*J.S.D.C.*, 75 (1959) 511) using both "natural" subjects and a controlled display consisting of 80 2-in. squares of 24 colours randomly distributed has led to the conclusion that the mechanism involved seems to be the addition of the filter colour and the colour produced by adaptation of the eye. This colour is not exactly complementary to the filter and permits production of hues arising from two-colour mixing between the approximate complement and the modulated colour-field caused by the filter. Probably some of the colours observed which could not have come from such mixtures might appear because of the effect of local colour surrounds. The process thus appears to be an interesting variation of a two-colour mixture system and suffers from all of the limitations thereof; specifically, failure to reproduce the full range of colours. Accordingly, Land's contention that conventional colour theory is inadequate to explain the observed effect does not seem justified. C.O.C.

### Colouring Mercuric Chloride Solutions

K. J. Steel

*Pharm. J.*, 183 (1959) 253

*Chem. Abs.*, 54 (10 March 1960) 5008

Sulphan Blue is suitable for colouring  $\text{HgCl}_2$  if the solutions are protected from light and heat. Saline solutions of  $\text{HgCl}_2$ , mercuric acetate, and mercuric cyanide can be coloured with Indigo Carmine (C.I. Acid Blue 74), Sulphan Blue or Trypan Blue. C.O.C.

# Aridye Aquadprint

## AQUEOUS PIGMENT PRINTING COLOURS

*for prints with a REALLY soft handle*  
particularly advantageous for printing on  
**NYLON & TERYLENE**

**FREEDOM from TACK**

*Eliminates danger of marking-off*

**QUICK DRYING**

*Allowing maximum production*

\* *Brilliant Shades*

\* *Low-cost Binder*

**White AL. for the best matt white**

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**TENNANTS TEXTILE COLOURS LTD.**

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The Society of Dyers and Colourists

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# ADVANCE ANNOUNCEMENT

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## Standard Methods for the Determination of the Colour Fastness of Textiles

The methods of fastness testing sponsored by the Society of Dyers and Colourists are published as a separate handbook under the title "Standard Methods for the Determination of the Colour Fastness of Textiles", the first edition appearing in 1955.

Developments in fastness testing, particularly internationally, necessitated the publication in 1958 of a supplement to the handbook and since then further developments have occurred. **Instead of issuing a second supplement, however, the Society's Fastness Tests Co-ordinating Committee decided that it would be more convenient for the Society to issue a Second Edition of Standard Methods for the Determination of the Colour Fastness of Textiles** which will shortly be available from the offices of the Society.

The Second Edition contains the tests, etc., which appeared in the *Journal* as Sponsored Publications since the supplement was published—

Light: Daylight at High Humidity

The use of fading lamps

Pleating and Setting

and also three tests which are now appearing for the first time—

Light: Daylight (U.S.A. Method)

Xenon lamp

Vulcanising: Hot air

Mainly in the interest of international agreement two of the original tests have been substantially modified: these are—

Burnt-gas fumes

Perspiration

whilst minor modifications have been made to certain others.

Many of the tests in the handbook have become Recommendations of the International Organisation for Standardisation and have been adopted as National Standards in many countries including the United Kingdom. A list of equivalent national standards is included in each test which should be of value where exports and imports are concerned.

To facilitate ease of reference, the tests have now been arranged alphabetically and a standard lay-out has been adopted.

**THIS HANDBOOK IS UNDOUBTEDLY THE MOST COMPREHENSIVE AND UP-TO-DATE SOURCE OF INFORMATION ON COLOUR FASTNESS TESTING IN THE WORLD AND IS INDISPENSABLE WHEREVER COLOUR FASTNESS TESTS ARE MADE.**

**Ensure receipt of an early copy by placing your order  
with the Society— NOW**

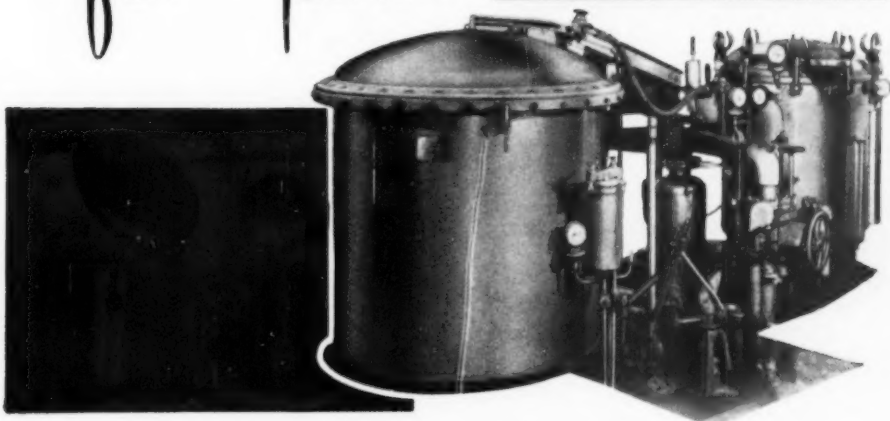
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# PEGG

## DYEING AND DRYING MACHINES

for Yarns

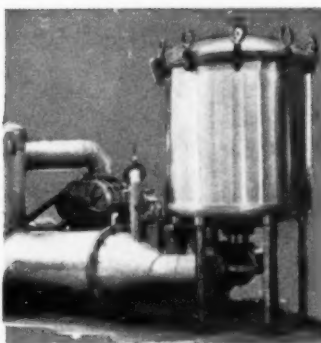


### HIGH-TEMPERATURE OR ATMOSPHERIC PRESSURE DYEING MACHINES

• • • •

To accommodate carriers for dyeing all types of natural and synthetic fibres in loose stock, tops, package, cone, beam or cake form.

• • • •

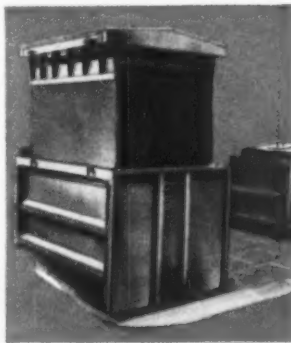


### PRESSURE DRYING MACHINE

Totally enclosed, re-circulating type to accommodate carrier loaded with tops, yarn in cheese or cone straight out of the dyeing machine.

### "PULSATOR" HANK DYEING MACHINE

For all class of wool, worsted, mixture and linen yarns, as well as ribbons, tapes, etc. Pulsating flow action ensures maximum penetration.



Builders of dyeing machines for loose stock, hanks, packages, piece-goods, fabric and hose; also finishing machines for all classes of circular knitted and warp loom fabrics and garments. Pre-boarding and finishing machines for nylon hose.



Bentley-Group

## *Quick Acting Pressure Covers*

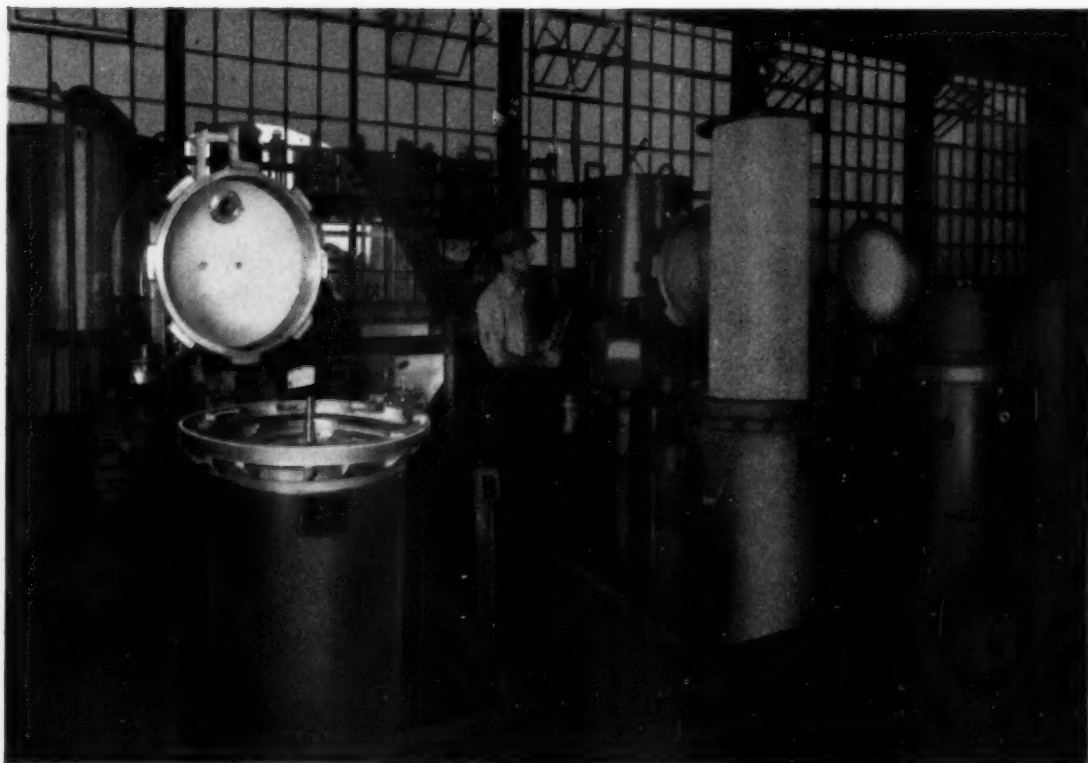
LONGCLOSE quick-acting pressure covers are available for various sizes of pressure dyeing and drying machines.

These covers are accurately counterbalanced and are secured and released by turning one handwheel only.

The sealing element is specially designed for safe and efficient operation independent of any external pressure source.

The illustration shows a coupled pair of LONGCLOSE High Temperature Single Beam Pressure Dyeing Machines fitted with quick-acting pressure covers.

*Fully descriptive literature sent on request.*



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Advertisements relating to APPOINTMENTS VACANT, APPOINTMENTS WANTED, and MISCELLANEOUS ITEMS are invited for insertion on this page. Advertisements of Appointments Wanted are gratis to members, but must not exceed twenty-four words.

All inquiries relating to Advertisements should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

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If you are interested, send details of your training and experience to the Managing Director, Stevensons (Dyers) Ltd., Amber Dye Works, Ambergate, Derbyshire.

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Amick, C. A., formerly of American Cyanamid Co., Bound Brook, New Jersey, U.S.A., to 121 East Maple Avenue, Bound Brook, New Jersey, U.S.A.

Bergman, Z., formerly of 1519 Sayre Street, Midland, Michigan, U.S.A., to 1519 Sayre, Midland, Michigan, U.S.A.

Ceritoglu, M., formerly of 197 Hyde Park Road, Leeds 6, Yorkshire, to 45 Brudenell Road, Leeds 6, Yorkshire

Cockshott, J. S., formerly of Dyehouse Department, I.C.I. Dyestuffs Division, Blackley, Manchester 8, Lancashire, to 8 Queen's Road, Bradford 8, Yorkshire

Daffern, A. D., formerly of 73 Oker Avenue, Darley Dale, Derbyshire, to 37 Bank Road, Matlock, Derbyshire

Douglas, C. D., formerly c/o The Yorkshire Dyeing & Proofing Co. Ltd., Spring Vale Works, Middleton, Lancashire, to J. Chadwick & Co. Ltd., Springbrook Works, Middleton Road, Chadderton, Oldham, Lancashire

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## NEW MEMBERS

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 Gleadale, J. M., 69 Malvern Road, Gillingham, Kent  
 Griffiths, J., 7 Patch Croft Road, Peel Hall, Wythenshawe, Manchester 22  
 Hampton, C. H., "The Glen", Southfield, Minchinhampton, near Stroud, Gloucestershire  
 Hardisty, D., 3 Tenby Close, Llanyravon, Cwmbran, Monmouthshire  
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 Hurlstone, S. F., Bernard Wardle & Co. Ltd., Whitehall Works, Chinley, via Stockport  
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 McCourt, W. K., 23 Cameron Street, Botanic Avenue, Belfast 7

McNab, I. O., CIBA Clayton Ltd., 157 Leeds Road, Bradford  
 Messer, A., 812 15 Street, Newport News, Virginia, U.S.A.  
 Shirt, C. V., Harpur Cottage, Welch's Lane, Chinley, near Stockport, Cheshire  
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 Sule, A. D., c/o Shri Ram Institute for Ind. Res., 19 University Road, Delhi 8, India  
 Vann, R. I., 38 Faire Road, Glenfield, Leicester  
 Wilson, J., British Cotton & Wool Dyers' Association Ltd., Central Laboratory, Cumberland Street, Manchester 3  
 Yarr, W. H. B., 18 Cooldarragh Park, Cavehill Road, Belfast 14.  
 Yates, T. G., 28 Britain Street, Bury, Lancashire

## MEMBERS' CHANGES OF ADDRESS—continued

Dronfield, E., formerly of 5 Manchester Road, Fairfield, Manchester, to 84 Mouldeth Road West, Withington, Manchester 20  
 Eland, V. E., formerly of "Suffolk Lodge", Bolton Avenue, Windsor, Berkshire, to "Puffins Ash", 63 Buckingham Road, Shoreham-by-Sea, Sussex  
 Grant, W. G. B., formerly of 8 Craigton Gardens, Milngavie, near Glasgow, to CIBA Clayton Ltd., Manchester 11  
 Habermehl, H. A., formerly of 1554 Leda Avenue, Port Credit, Ontario, Canada, to Box 173, Hespeler, Ontario, Canada  
 Harding, A. J. I., formerly of "Belmont", Goodes Avenue, Syston, Leicester, to Box 39, G. Post Office, Spartanburg, S. Carolina, U.S.A.  
 Hawkes, J. A., formerly of 74 Seagrave Road, Sibley, near Loughborough, Leicestershire, to 96 College Road, Syston, Leicestershire  
 Hobson, B., formerly of 30 Lee Road, Lee Estate, Ravenshorpe, Dewsbury, Yorkshire, to c/o Mrs. Forsyth, 25 Kettle Green Road, Clackmannan, Clackmannanshire, Scotland  
 Ingham, P., formerly of 17 Chapel Lane, Yeadon, Leeds, to 40 Hawthorn Road, Yeadon, near Leeds  
 Janczarek, R., formerly of 41 Parks Street, Coventry, Warwickshire, to 18 The Green, Attleborough, Nuneaton, Warwickshire  
 Jennings, A. H., formerly of 14 Marston Gardens, Luton, Bedfordshire, to "Hunters Lodge", Keymer Road, Burgess Hill, Sussex  
 Kennedy, J. G., formerly of 101 Campden Hill Road, London W8, to Flat B, 63 Belsize Park Gardens, London NW3  
 Kitchen, J. B., formerly of I.C.I. Central Work Study Dept., Imperial Chemical House, Millbank, London SW1, to Personnel Director, Imperial Chemical Industries Ltd., Plastics Division, Black Fan Road, Welwyn Garden City, Hertfordshire  
 Lee, J. G., formerly of 42 Pawson Street, Morley, near Leeds, to Meal Hill Cottage, New Mill, Huddersfield  
 Lockwood, R., formerly of 25 Cobcroft Road, Fartown, Huddersfield, to Richmond House, 2 Richmond Avenue, Fartown, Huddersfield  
 McDonald, R., formerly of 5 Orchard Street, Paisley, Renfrewshire, to "Westlea", 24 Methuen Road, Paisley, Renfrewshire  
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 Malouf, Amin, formerly of Arassa 577, Alwiyah, Baghdad, Iraq, to c/o Samhry Bros. Co. Will., Baghdad, Iraq  
 Marsh, F. H., formerly of 21 Fearnville View, Leeds 8, to Nichol End, Ling Lane, Scarcroft, near Leeds  
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 Raper, D. P., formerly of 7 Harboro' Road, Sale, Cheshire, to Casita, Chapel Lane, Hale Barnes, Cheshire  
 Richardson, H. H., formerly of Shell Chemical Co. Ltd., 105/109 Strand, London WC2, to Messrs. R. S. Waddington Ltd., 35 West Hill, London SW18  
 Sanderson, R. I. S., formerly c/o Kooros Bros., P.O. Box 1547, Tehran, Iran, to P.O. Box 451, Tehran, Iran  
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 Starkie, Jas., formerly of Messrs. Brotherton & Co. Ltd., Port Rainbow, New Ferry, Birkenhead, to 42 Allport Road, Bromborough, Wirral, Cheshire  
 Sykes, J. A. W., formerly of 39 Woodhouse Lane, Brighouse, Yorkshire, to Rush Common House, Appleford Drive, Abingdon, Berkshire  
 Taylor, T. P., formerly of 534 Wilbraham Road, Chorltoncum-Hardy, Manchester 21, to 12 Finney Lane, Cheadle, Cheshire  
 Terrington, D., formerly of Shri Digvijaya Woollen Mills Ltd., Aerodrome Road, Jamnagar, India, to Himat Villa, Bedi Road, Jamnagar, Sarashtra, India  
 Trafford, F. B., formerly of 1036 Bury Road, Brightmet, Bolton, Lancashire, to 18 Falkland Road, Brightmet, Bolton, Lancashire  
 Valentine, Dr. L., formerly of Research Department, Tootal, Broadhurst Lee Co. Ltd., Oxford Street, Manchester 1, to The Paint Research Station, Waldegrave Road, Teddington, Middlesex  
 Walker, J., formerly of 415 Worsley Road, Winton, Eccles, Manchester, to 33 Greenleach Lane, Worsley, near Manchester  
 Walker, S. G., formerly of Greengates, Toome Road, Randalstown, Co. Antrim, Northern Ireland, to Islamabaun, Muckamore, Co. Antrim, Northern Ireland  
 Whitelaw, C. D., formerly of 1 Hillside Road, Dundee, Angus, to I.C.I. Thornton House, Bridge Street, Bradford  
 Wilson, C. T., formerly of 6 "Stray View", Leeds Road, Harrogate, Yorkshire, to c/o Timarn Worsted & Woollen Co. Ltd., Timarn, South Island, New Zealand  
 Yamaya, W., formerly c/o Research Laboratory Mitsubishi Chemical Ind. Ltd., 290 Hisamoto Kamoi-Cho, Kawasaki-Shi, Kanagawa-Pref., Japan, to c/o Research Laboratory, Mitsubishi Chemical Ind. Ltd., Mizono-kuchi, Kawasaki-Shi, Kanagawa-Pref., Japan  
 Zollinger, Dr. H., formerly of 9 Im Marteli, Binningen, Switzerland, to Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, Universitätsstrasse 6, Zurich, Switzerland





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